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12th International Conference on Carbonaceous Particles in the Atmosphere

03.-06.04.2019, Vienna (Austria)

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12th International Conference on Carbonaceous Particles in the Atmosphere

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ÖSTERREICHISCHE AKADEMIE DER WISSENSCHAFTEN



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Chapter 1 Orals

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- 1.7 Carbonaceous CCN and INPs
- 1.8 Optical properties of carbonaceous aerosols, radiative forcing and climate

1.1 Secondary organic aerosol formation

1-1 Implications of photochemical ageing for source apportionment and health effects of wood combustion aerosol

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The combustion of logwood in residential stoves has been identified as substantial contributor to local air pollution. It releases high levels of particle-bound polycyclic aromatic hydrocarbons (PAH) and oxygenated PAH (OPAH), in the range of 0.1% - 1% of the total emitted particulate matter (PM). However, in the atmosphere those compounds undergo chemical transformation along with physical transformation of PM, which changes the toxicity of wood combustion emissions. Degradation kinetics of particle-bound PAH and OPAH are mainly affected by the particle composition and microstructure. Gas phase PAH, in contrast, have higher differences in reactivity with OH, O₃ and NO₃ and are less affected by direct photolysis.

In this study, we aged combustion aerosol from spruce logwood with a recently described highflow oxidation flow reactor, "Photochemical Emission Aging flowtube Reactor" (PEAR) (Ihalainen et al. (2019), Aerosol Science & Technology) and investigated the effect of ageing on emissions of PAH and OPAH as well as PAH diagnostic ratios for emission source identification. Moreover, genotoxicity of primary and aged emissions were assessed in 4 h *in vitro* exposures of A549 cells by comet assay. Finally, carcinogenity of the emissions based on PAH toxicity equivalent (PAH-TEQ) was determined and compared to emissions from a non-road diesel engine as reference for carcinogenic emissions "group 1".The combustion of spruce logwood released 404 μ g MJ⁻¹ of 35 analysed PAH and 299 μ g MJ⁻¹ of 10 analysed OPAH, most of which are known potential mutagens and carcinogens. Photochemical processing by PEAR substantially degraded particle-bound PAH, which was also reflected in declining PAH-TEQ by 45 to 80% per equivalent day of photochemical ageing. However, the wood combustion aerosol would require more than four days of photochemical ageing to reach comparable TEQ of diesel exhaust particles, a carcinogen of "group 1", from a 24.5 kW non-road diesel engine. Compared to PAH, OPAH were less affected by photochemical ageing, supposedly due to secondary formation.

Genotoxicity increased significantly from clean air control to both primary and aged aerosol as assessed by comet assay. However, despite substantial degradation of carcinogenic PAH, the genotoxicity between primary and aged spruce combustion aerosol remained comparable. Furthermore, exposure to filtered primary and aged aerosol decreased the DNA damage, but not with a significance level below 5%, which highlights the importance of the gas phase for the underlying cellular mechanisms.

Diagnostic ratios to identify wood combustion emissions in ambient air remain stable during photochemical ageing for PAH species PHE/ANT, FLA/PYR, RET/CHR, and IcdPYR/BghiPER. On the other hand, BaP/BeP and BaA/CHR allow monitoring of the photochemical age.

This study motivates more detailed investigation of the consequences of photochemical ageing on toxicity and identification of wood combustion emissions in ambient air.

1-2 The intriguing role of nitrous acid in atmospheric aqueousphase formation of nitrocatechols under nighttime conditions

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Secondary organic aerosols (SOA) constitute a significant proportion of ambient particulate matter and are well-known to have adverse effects on air quality and human health. SOA formed in the atmosphere and atmospheric brown carbon (BrC) as a significant SOA constituent represent key uncertainties in determining the impact of aerosols on climate, in part due to their complexity and continually changing composition. Besides, dynamic mechanisms of SOA formation and aging are poorly understood. It has been thought that SOA are formed from gas-phase oxidation followed by adsorption of semi-volatile products into pre-existing particles [1]. Recent studies have indicated that chemical processes in the atmospheric aqueous phase can also efficiently contribute to SOA formation [2].

Besides many short-lived radicals, non-radical oxidants such as nitrous acid (HNO_2) can also take an important part in atmospheric aqueous-phase transformation. The role of HNO_2 in the atmospheric waters is not yet clear, but its importance as a catalyst in condense-phase aromatic nitration has already been emphasized [3]. Aromatic compounds, on the other hand, contribute significantly to the budget of atmospheric pollutants.

In the present study, the intriguing role of HNO_2 (catalytic and oxidative) in the dark transformation of 3-methylcatechol under atmospherically relevant aqueous-phase conditions is emphasized. Three possible pathways of dark 3-methyl-5-nitrocatechol and 3-methyl-4-nitrocatechol formation, markedly dependent on reaction conditions, were considered. In the dominant pathway, HNO_2 is directly involved in the transformation of 3-methylcatechol *via* consecutive oxidation and conjugated addition reaction. Under very acidic conditions, the other two nitration pathways, oxidative aromatic nitration (electrophilic) [4] and recombination of radical species, gain in importance. These results highlight the significance of catechol oxidation-conjugated addition reaction in nighttime secondary nitoaromatic chromophore formation.

Reference

- [1] J. F. Pankow (1994), Atmos. Environ. 28, 189-193
- [2] B. Ervens, B.J. Turpin, R.J. Weber (2011), Atmos. Chem. Phys. 11, 11069-11069
- [3] B. D. Beake, J. Constantine, and R. B. Moodie (1994), J. Chem. Soc., Perkin Trans. 2, 335-340
- [4] A. Kroflič, M. Grilc, and I. Grgić (2015), Environ. Sci. Technol. 49, 9150-9158

1-3 Online quantification of Reactive Oxygen Species (ROS) in atmospheric aerosol: results from field and laboratory experiments

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Epidemiological studies have llinked atmospheric aerosol levels with mortality and hospital admissions due to respiratory and cardiovascular disease. It is often hypothesised that these negative health effects are due to particle-bound reactive oxygen species (ROS). Established methods to quantify ROS mostly rely on particles being collected on filters, followed by subsequent extraction steps and chemical analysis. These methods usually have time resolutions of hours to days, which can limit the comparison with other fast changing components in the atmosphere. In addition, a long delay between collection of particle-bound ROS and their analysis might underestimate true total ROS concentrations because many ROS components may be highly reactive and thus short-lived.

To overcome these limitations, we developed an instrument to allow on-line, continuous measurement of particle-bound ROS using the fluorescence probe 2'7'-dichlorofluorescein (DCFH), in conjunction with horseradish peroxidase (HRP), via fluorescence spectroscopy. A high time resolution of about 5min allows tracking fast changes in the atmosphere e.g. changes in meteorological conditions or traffic pattern. We show that up to 40-80% of ROS in organic aerosol has a short lifetime of only about 15min, emphasising the need for fast online techniques to obtain reliable ROS quantification data. We will also present a similar online instrument that determines the oxidative potential of atmospheric particles by quantifying the reactivity of aerosol components towards ascorbic acid, an anti-oxidant naturally present in the lung.

We will discuss online ROS analyses of secondary organic aerosol generated in laboratory chamber experiments and compare these with ambient urban measurements. Seasonal variations are discussed as well as diurnal cycles with maxima developing in summer in later afternoon whereas winter daily maxima usually occur around midday or early afternoon. These online data will also be compared with offline ROS analysis to highlight the differences of these two measurement approaches.

1.2 Analytical techniques and methods

2-1 Application of Spin Traps to Detect Reactive Intermediates and Reactive Oxygen Species in Secondary Organic Aerosol

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The chemical composition and evolution of secondary organic aerosol (SOA) in the atmosphere represents one of the largest uncertainties in our current understanding of air quality. Studies suggest that reactive oxygen species (ROS), either present in ambient aerosol and exogenously delivered or generated by particle components *in vivo*, are potentially a major contributor to aerosol toxicity. Several methods are currently available for probing ROS concentrations in aerosol, however, the role of radicals and reactive intermediates in both the formation and ageing of aerosol, as well as their contribution to the health-relevant properties of ambient aerosol, at present remains highly uncertain. Recently, a study by Stevanovic *et al.1* introduced the profluorescent spin trap BPEAnit (9,10-bis-(phenylethynyl)-anthracene-nitroxide), where they subsequently used this method to quantify particle-bound radicals in aerosol generated from the combustion of biomaterial and fuel.

In this work, BPEAnit is applied to study the concentrations of particle-bound radicals in SOA. Radical concentrations were estimated for SOA generated from the ozonolysis of α -pinene, β -caryophyllene and limonene in a flow tube, to probe the assays response to SOA formed from biogenic volatile organic compounds. SOA is captured in an impinger containing BPEAnit/DMSO, before subsequent analysis using fluorescent spectroscopy. Using this method, a pseudo-1st order rate constant of $k = 7.3 \pm 1.7 \times 10-3$ s-1 was derived for the overall decay of organic radicals in apinene SOA, implying a radical lifetime on the order of several minutes. Furthermore, building on our recent work in Giorio *et al.*,2 the spin trap PBN (*N-tert*-butyl- α -phenylnitrone) was used to trap Criegee intermediates (CIs) present in the aerosol phase, with the resulting adducts analysed using high performance liquid chromatography high-resolution mass spectrometry. Experiments were conducted with this method using SOA generated from β -caryophyllene ozonolysis in a flow tube, demonstrating the technique's unique capability to detect multiple CIs present in SOA and representing the first detection of CIs in organic aerosol. Detected CIs were estimated to constitute approximately 0.8% of the total particle mass, demonstrating the potential of this method to provide quantitative data of condensed phase CIs.

2-2 Chemical characterization of laboratory-generated tar ball particles

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Atmospheric tar balls (TBs) belong to the family of *Brown Carbon* (BrC) emitted by biomass burning. Albeit TBs have been shown to be abundant in the troposphere, very little is known about their distinct chemical properties because in biomass smoke TBs coexist with various other particle types and cannot be studied by bulk analytical methods. Only single particle analyses available with electron microscopy have been able to reveal some of their characteristics.

In this work the chemical properties of laboratory-generated tar ball particles (Lab-TBs) produced from wood tars of three tree species in the laboratory were investigated by analytical techniques had never been used before for their direct chemical analysis. The elemental compositions of Lab-TBs from three wood species were very similar to one another and to those characteristic of atmospheric TBs collected from savanna fires during SAFARI 2000 sampling campaign. The O/C and H/C molar ratios of the generated Lab-TBs were close to those found in soot particles. On the other hand, the FT-IR spectra of the Lab-TBs shared some similarities with those of humic-like substances (HULIS). The FT-IR measurements indicated that the oxygen atoms of Lab-TBs are mainly associated with hydroxyl and keto functional groups. Whereas Raman activity was not detected in the wood tars in the range of 1000-1800 cm cm-1, the Raman spectra of TBs were dominated by two pronounced bands with intensity maxima near 1580 (G band) and 1350 cm-1 (D band), indicating the presence of sp2-hybridized carbon structures and disorder in them, respectively. In the Py-GC-MS chromatograms of the Lab-TBs mostly aromatic compounds were identified in accordance with the results of Raman and FT-IR spectroscopy. According to organic carbon/elemental carbon (OC/EC) analysis (using EUSAAR 2 protocol), 22% of the total carbon content of Lab-TBs was identified as EC. Our results suggest that spherical atmospheric TBs with low O/C molar ratios are closer to BC in many of their properties than to weakly absorbing HULIS.

This work was supported by the project GINOP-2.3.2-15-2016-00055. This work was also supported by the János Bolyai Research Scholarship of the Hungarian Academy of Sciences.

2-3 Micro-Raman Spectroscopy as a vibrational probe to reveal soot nanostructure

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With an industry traffic forecast showing that airlines are welcoming a year-over-year increase of passengers, the airline industry keeps contributing to the intensification of emissions of solid particles in the atmosphere. These particles are involved in many physical and chemical processes that can affect the atmospheric radiative forcing (Lee et al. 2010), or even the formation of clouds and their lifetime expectancy. Our work focuses on aircraft soot particles analogs, i.e., particles similar to those emitted by aircraft engines during the incomplete combustion of kerosene fuel (Parent et al. 2016). These particles, once released in the troposphere, can act as nucleating agents and promote the formation of ice crystals. Hence, they may help in the formation of contrails that may persist and further evolve into cirrus clouds. To interpret ice nucleation activities of various soot samples, detailed analyses of their physico-chemical properties (structure and chemical composition) are needed beforehand and were performed using Raman micro-spectrometry. The goal is to establish a link between the physicochemical properties of soot particles and their ice nucleation activity.

In this work, we used micro-Raman spectroscopy (at 514 nm excitation wavelength) to characterize soot particles produced by either a kerosene flame or a combustion Aerosol Standard (CAST) burner supplied with various propane-air mixture ratios (different set points) and producing soot samples with a wide range of organic carbon to total carbon ratios (OC/TC). The analysis of the first-order Raman bands of these soot samples is based on the deconvolution model proposed by Sadezky et al. (2005) and/or that of Ferrari and Robertson (2000). Deconvolution of Raman spectra allowed the monitoring of spectral parameters (position, full width at half maximum (FWHM), D1 to G height/area ratio) and their evolution with the nanostructure or chemical composition in soot samples of different origin or set points.

Acknowledgments: This work was supported by the CORAC MERMOSE project, funded by French Civil Aviation Authority (DGAC) and by the French National Research Agency (ANR) through the PIA Programme d'Investissement d'Avenir) under contract ANR-10-LABX-005 (LABEX CaPPA-Chemical and Physical Properties of the Atmosphere) and the CLIMIBIO project via the Contrat de Plan Etat-Région of the Haut-de-France region. The authors acknowledge E. Therssen (PC2A) and F.-X. Ouf (IRSN) for providing Kerosene and CAST soot samples.

References:

Lee, D.S., et al. (2010). Atmos. Environ, 44, 4678-4734. Parent., P., Laffon, C., Marhaba, I., Ferry, D.,Regier, T.Z., Ortega, I.K.Chazallon, B., Carpentier, Y.,Focsa, C. (2016) Carbon, 101, 86-100. Sadezky, A., Muckenhuber, H., Grothe, H., Niessner, R., Poschl, U. (2005). Carbon, 43, 1731-1742. Ferrari, A.C. & Robertson, J.(2000), Phys. Rev. B, 61(20), 14095.

2-4 Secondary ion mass spectrometry and combustion: finding trends in soot nucleation and growth

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Among the many pollutants produced from the incomplete combustion of hydrocarbons, soot has a dramatic impact on both the environment and the human health and activities. Understanding the transition from the gas phase precursors to the very first particles in the condensed phase (*soot nucleation*) is an important step toward controlled and cleaner combustion (D'Anna 2009, Wang 2011).

To obtain information on the soot nucleation process in flames, an original experimental approach is proposed based on the chemical analysis of nascent soot particles and their precursors in parallel. In-situ laser induced incandescence/fluorescence is used to map the soot particles and precursors in flame. Soot and the gas phase are then sampled at different reaction time (microprobe extraction followed by impaction on wafers), and high resolution secondary ion mass spectrometry is performed to identify the molecular precursors of soot in the gas phase and the compounds adsorbed on the surface of the nascent particles. The results of the analysis of a large database of 152 samples extracted from four laboratory methane flames (two low pressure premixed flames and two atmospheric diffusion flames) are shown and discussed. Multivariate statistical methods (principal component analysis and hierarchic data clustering) are applied to reduce the high dimensionality of the database and to reveal hidden trends. The complete characterization of the experimental methodology (Irimiea 2018) and a detailed discussion based on the ensemble of the collected data (Irimiea 2019) have been recently reported.

The proposed analytical approach is able to provide important information like the mass range of the hydrocarbons involved in soot nucleation. In particular, the comparison of the mass spectra obtained from a nucleation and a sooting premixed flame shows that the compounds involved in soot nucleation can be as small as polycyclic aromatic hydrocarbons having 2-3 aromatic rings and include 5 member rings. The comparison of the experimental data with the predictions of kinetic modeling shows that the growth process of the most stable hydrocarbons follows the most compact of all the possible structures. Oxygen containing hydrocarbons are only found associated to soot nucleation in the diffusion flames, while they are virtually absent from the pool of molecules associated to soot nucleation in the premixed flames. The output of this work provides a detailed list of compounds to be considered for future advancements in kinetic modeling in combustion.

D'Anna, A. Proc. Combust. Inst. 32 (2009) 593-613.

Wang, H., Proc. Combust. Inst. 33 (2011) 41-67.

Irimiea, C., Faccinetto, A., Ortega, I. K., Carpentier, Y., Nuns, N. Therssen, E., Desgroux, P., Focsa, C., Rapid Commun. Mass Spectrom. 32 (2018) 1015-1025.

Irimiea, C., Faccinetto, A., Ortega, I. K., Mercier X., Nuns, N. Therssen, E., Desgroux, P., Focsa, C., Carbon (2019) under review.

2-5 Exploiting the features of multi- λ polar photometers to retrieve optical properties of aerosols collected on filters

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In the last years, an increasing interest has been paid to the knowledge of aerosol optical properties due to the large uncertainties still affecting the estimates of the role of aerosols in the Earth radiative forcing. In this frame, a number of instruments - both in-situ and filter-based – have been developed to retrieve a robust assessment of the aerosol absorption coefficient, possibly at multi wavelengths. At the state-of-art there is not a gold reference standard and results from intercomparison exercises among the most widely used instruments still underline significant differences and the need of correction algorithms, although many of these commercial instruments are currently used in monitoring networks and research field campaigns. Moreover, in many field campaigns a huge amount of filters is collected for aerosol chemical-physical characterisation but optical absorption properties are usually not included.

The research groups of the Universities of Milan and Genoa have developed benchtop multi- λ polar photometers[1,2,3] (called PP_UniMI and MWAA, respectively) which allow the off-line determination of the absorption coefficient (babs) of particles collected, in principle, on any kind of filters; in addition, PP_UniMI has been implemented to characterise optical properties on 1-h resolution samples collected by streaker samplers[2]. It is noteworthy that PP_UniMI and MWAA allow also retrospective analysis on stored filters thus retrieving e.g. data of climatological interest.

The measurement methodology relies on the direct measurement of the phase function in the scattering plane and retrieves babs from the application of the adding method and a radiative transfer model to account for multiple scattering, i.e. the same algorithm used by the MAAP (Multi-Angle Absorption Photometer[1,3]). Tests on PP_UniMI and MWAA reliability have been performed vs. filter-based instrumentation (i.e. MAAP) with ambient samples and vs. both in-situ and filter-based measurements in laboratory tests[4]. Multi-l measurements of babs by PP_UniMI have been carried out in a number of field campaigns and results will be shown for selected case-studies including also optical source apportionment.

More recently, the polar photometers have been implemented to measure filter spots taken from MAAP and Aethalometer aiming at clarifying the causes underneath the disagreement found between babs obtained by different instrumentation during recent field campaigns[5]. Moreover, the availability of multi-l measurements of filter spots can be used to investigate correction factors used e.g. the enhancement C factor in the Aethalometer AE33, their dependence on the wavelength and on the aerosol chemical composition.

2-6 The Single Particle Soot Photometer - Extended Range (SP2-XR) for black carbon measurements: an extensive comparison with the SP2

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Black carbon (BC) aerosols have important climate impacts because they are the most efficient light absorbing aerosol in the Earth's atmosphere. It is estimated that BC is the second anthropogenic climate-forcing agent behind only CO2 (at an uncertainty level of 90%).

To assess the climate impacts of BC it is critical to develop sensitive, field-deployable instrumentation for measuring BC mass concentrations and size distributions. The *Single-Particles Soot Photometer* (SP2, DMT) is a single particle instrument using the laser-induced-incandescence technique. A high intensity Nd:YAG laser beam (λ =1064 nm) heats each BC particle up to 4000 K where an incandescence signal is emitted before vaporizing. The intensity of the signal is proportional to the mass of the *refractory* BC (rBC) particle and this relation is known via an empirical calibration. The SP2 approximately covers the size range from 90 to 600 nm BC mass equivalent diameter.

The SP2 is a well-established and characterized instrument that has been deployed in many laboratory studies and field campaigns to shed light on the mass/number concentrations and size distribution of BC particles (e.g. Laborde et al., 2012)

The *Single-Particles Soot Photometer Extended-Range* (SP2-XR) is a new instrument from DMT designed to be more "user-friendly" and to have a wider size detection range. The SP2-XR is based on the same physical principles as the SP2 but has many "practical" advantages making it suitable for long-term monitoring campaigns. The raw data are automatically processed providing real-time results for rBC particle number/mass concentration and size distribution. It is smaller, lighter (13 kg), it has only two detectors instead of four (broadband incandescence and scattering) and the data acquisition was improved.

In this study, the performance of the SP2-XR was evaluated and compared to that of the SP2 during laboratory and field measurements: stability of the calibration curve and response to different calibration materials, size-resolved detection efficiency (DE) and integrated BC mass concentration and size distribution.

The SP2-XR has a clearly better signal-to-noise ratio in quantifying the mass of very small BC cores, however, the threshold at which detection efficiency drops below unity is comparable to the original SP2. The XR incandescence calibration curves show good stability over time and the relative sensitivity to fullerene soot and Aquadag calibration aerosols is comparable with that of the SP2. The rBC mass/number concentrations and size distributions measured by the two instrument variants are in remarkable agreement across both field campaigns and laboratory measurements. In conclusion, our results show that the SP2-XR BC data agree with those inferred from the broadband channel of the SP2, thus making it a valid alternative to the SP2.

Laborde, M., et al., Single Particle Soot Photometer intercomparison at the AIDA chamber, Atmos. Meas. Tech., 22, 2012.

2-7 Assessment of Light Absorbing Carbon measurements on PTFE filters by the Multi-wavelength Absorption Black Carbon Instrument (MABI)

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Source apportionment studies are based in the various chemical fingerprints of aerosol species originating from different sources. The detailed analysis and chemical characterization of aerosol samples collected on filters is the common practice for the identification of several major and trace metals, ions and organic tracers with their concentrations ranging over several orders of magnitude. In many instances, where real time data for black carbon are not available, there are limitations obtaining information for the carbonaceous fraction usually concerning the filter material. The Multi-wavelength Absorption Black Carbon Instrument (MABI) introduced by ANSTO (Cohen et al., 2000) is a non-destructive optical transmission method for deriving equivalent Black Carbon mass (eBC) on Teflon filters. It is based on a basic principles calibration taking into account a welldefined mass absorption coefficient and has been used extensively in source apportionment studies. A primary standard for aerosol absorption is lacking due to problems associated with the optical response of aerosol particles embedded in filter material and the high variability and uncertainty of mass absorption coefficients (Petzold et al., 2013). An intercomparison study was performed in Athens, in order to assess the MABI response with respect to concurrent measurements by well known field instruments for aerosol absorption and eBC. In general a very good correlation among the different techniques is observed for a variety of aerosol loads in the Demokritos suburban station in Athens. The observed variability is discussed in view of current state of the art knowledge regarding source aerosol types and filter loading.

References

Cohen, D.D. Taha G., Stelcer, E., Garton, D., Box. G., (2000) The Measurement and Sources of Fine Particle Elemental Carbon at Several Key Sites in NSW over the Past Eight Years, 15th International Clean Air Conf., 27-30 November 2000, Sydney, Australia

Petzold, A.; Ogren, J.A.; Fiebig, M.; Laj, P.; Li, S.-M.; Baltensperger, U.; Holzer-Popp, T.; Kinne, S.;

Pappalardo, G.; Sugimoto, N.; et al. Recommendations for the interpretation of "black carbon" measurements. Atmos. Chem. Phys. 2013, 13, 8365–8379.

2-8 Comparison of co-located rBC and EC mass concentration measurements from field campaigns at several European sites

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Black carbon (BC) is commonly defined as the insoluble, refractory and strongly light-absorbing component of particulate matter consisting primarily of graphene-like sp2-bonded carbon. When it comes to measurements, "BC mass" is defined operationally through methodologies that use distinct BC properties in order to quantify it.

BC mass concentration has traditionally been detected with two methods: as elemental carbon (EC) measured by thermal-optical evolved gas analysis and as equivalent black carbon (eBC) when BC mass is derived from absorption coefficient measurements. Over the last decade, campaign-based Single-Particle Soot Photometer (SP2) measurements of refractory black carbon (rBC) mass concentrations have become more common. Thermal-optical analysis is still the most used technique in monitoring networks; however even with optical correction EC measurements can be biased by OC pyrolysis. Moreover, the existence of many different thermal evolution protocols can result in an elemental carbon-to-total carbon bias of up to a factor of five. For this reason, an optimized thermal evolution protocol (EUSAAR_2) has been defined for European sites. The SP2 detects rBC mass without interferences from other internally- or externally-mixed particulate matter, and performs quantification based on an empirical calibration. This calibration may vary between BC samples by as much as 9%, if the chemical microstructure of the BC varies substantially.

Only a limited number of studies have assessed the level of agreement between different EC and rBC mass concentration measurements and the reasons behind any discrepancies. Therefore, in this work several co-located EC and rBC data sets from previous field campaigns (including already published ones) across several European sites (Paris; Bologna; Cabauw and Melpitz) have been collated and examined. All EC measurements were performed with the EUSAAR_2 thermal protocol and all rBC measurements were performed with SP2s calibrated with the same standard material. The aim of the intercomparison is to identify the differences between BC mass concentrations measured by the two techniques and the reasons behind these differences (e.g. calibration biases, measurement artefacts).

The preliminary analysis found moderate to good correlation between rBC and EC mass concentrations measured at all the sites. However, the ratio of rBC/EC mass concentrations varied from 0.5 to 2. During the summer campaigns in Cabauw and Bologna, rBC concentrations were both on average 50% lower than corresponding EC concentrations. rBC concentrations were on average a factor of two higher and 20% higher than EC concentrations during the Melpitz winter and summer campaigns, respectively. Excellent agreement (within 5%) was found in Paris during winter. Further quality checks of these results are ongoing. The final intercomparison results will be presented along with a detailed discussion of the implications of the findings.

2-9 On-road chasing method evaluation with PEMS

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The on-road chasing method is one of few methods for the determination of real-world emission factors (EF). It has been used around the world in USA, China and Europe for EF determination (Canagaratna et al., 2004; Herndon et al., 2005; Schneider et al., 2008; Shorter et al., 2005; Wang et al., 2011, 2012, Ježek et al. 2015a). Its advantages over tunnel or remote sensing measurements are that you can see how the EF is changing in time and obtain EF distribution (Ježek et al. 2015 a,b) of individual vehicle as oppose to one point in time or a fleet average EF. Compared to Portable Emission Measurement System (PEMS) the method is less precise. The highest uncertainty of the method lies in the background determination (Ježek et al., 2015b). Nonetheless the method is less labor intensive and less time consuming than PEMS. With this method 100 of vehicles EF can be measured per day in real driving conditions. Therefore, it could be used as a monitoring tool for city or state authorities to find the so-called super-emitters - vehicles in the fleet that contribute disproportional amount to total fleet emissions.

We used the chasing method to measure emissions of a vehicle that was equipped with PEMS. We wanted to see how much the results of the two methods differ; and based on the comparison of the two methods, we wanted to set robust boundaries on the chasing method data processing algorithm developed for the MECEDES project in a way that also an inexperienced user could use the method to find super-emitters.

In our measurements we used an older diesel vehicle on which we installed AVL and Semtech PEMS (measuring PM, soot, CO2, other gases, engine variables, vehicle location and speed). The chasing platform was equipped with aethalometer AE33, Carbocap GMP 343 and a GPS. The measurements were made on March 23rd, 2018, in different speed regimes (30 - 90 km/h). The EF were calculated as EF= $\int BC/\int [C]^*wc$, where BC is either soot measured with PEMS or BC measured with the chasing platform, C is carbon in CO2 and wc is carbon fraction in fuel (0.87). With PEMS we calculated EF with 5s running integration window. In the chasing method we first subtracted the background measurements and calculated the EF with 3s running integration window (similar as Ježek et al., 2015).

The results show that the two method yield similar results. The dynamics of the two EF is very close, even though PEMS EF is more detailed while the chasing method is a more smoothed version of the signal. Statistically the EF distribution of the chasing method results in overall higher EF than the PEMS method. We will discuss what are the differences between the results of the two methods and discuss constraints that may be applied to the chasing method in order to get most robust and representative vehicle EF. We have tested the assumption of the same dilution of pollutants, and how the distance between the two vehicles affects the EF.

2-10 Organic matter exchange at the cryosphere-atmosphere interface

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Organic matter (OM) in the cryosphere originates from different sources (e.g. oxidation products of anthropogenic, biogenic, and biomass burning VOCs), is transported from short and long distances and is deposited via dry or wet deposition. Deposited on the snow surface, OM makes a unique proxy for the past air composition analysis; however, many challenges need to be addressed in order to reconstruct the past atmosphere. The recent development of TD-PTR-MS and its application to the analyses of aqueous samples allowed high-resolution data and needed means for assessing the atmosphere-cryosphere OM exchange. Using this method, we analysed high-altitude surface snow taken near Sonnblick Observatory, Austria in the late winter-spring 2017. Total organic ions composition changed in such a way that concentrations were increasing in a dry period and suddenly dropping with the fresh snow. The composition of OM between wet and dry deposition is also largely affected. We noticed distinctive groups of ions with similar concentration trend over that time, with suggesting common sources, chemistry processes, or transport pathways. The largest two groups of ions came from (a) surrounding forests (e.g. pinonic acid – associated with monoterpene oxidation) and (b) residential fires (levoglucosan - common biomass burning marker). We approximated the dry deposition of OM using a mass balance model and got a deposition rate of D = 206 ng mL-1day-1and a first-order loss rate constant k = 0.31 day-1. Calculated deposition velocities were inconsistent with the idea that organic aerosols contribute the bulk of deposited OM, instead, we suggest a dominant contribution of gas-phase sVOC over the OA in the total bulk organic matter. This all indicates that, at least for this site and location, snowatmosphere DOM exchange processes are mostly driven by gas-phase sVOCs, for which equilibration with air is fast, which has implications for the reconstruction of recent atmospheric conditions. In this work we will also investigate impact of different meteorological conditions on the deposition and composition of the OM retained in the snow.

2-11 Twin-plate ice nucleation assay (TINA) with infrared detection for high-throughput droplet freezing experiments with biological ice nuclei in laboratory and field samples

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For efficient analysis and characterization of biological ice nuclei under immersion freezing conditions, we developed a Twin-plate Ice Nucleation Assay (TINA) for high-throughput droplet freezing experiments, in which the temperature profile and freezing of each droplet is tracked by an infrared detector. In the fully automated setup, a couple of independently cooled aluminum blocks carrying two 96-well plates and two 384-well plates, respectively, are available to study ice nucleation and freezing events simultaneously in hundreds of microliter range droplets (0.1-40 μ L). A cooling system with two refrigerant circulation loops is used for high-precision temperature control (uncertainty < 0.2 K), enabling measurements over a wide range of temperatures (~272-233 K) at variable cooling rates (up to 10 K min-1).

The TINA instrument was tested and characterized in experiments with bacterial and fungal ice nuclei (IN) from *Pseudomonas syringae* (Snomax®) and *Mortierella alpina*, exhibiting freezing curves in good agreement with literature data. Moreover, TINA was applied to investigate the influence of chemical processing on the activity of biological IN, in particular the effects of oxidation and nitration reactions. Upon exposure of Snomax® to O3 and NO2, the cumulative number of IN active at 270-266 K decreased by more than one order of magnitude. Furthermore, TINA was used to study aqueous extracts of atmospheric aerosols, simultaneously investigating a multitude of samples that were pre-treated in different ways to distinguish different kinds of IN. For example, heat treatment and filtration indicated that most biological IN were larger than 5 μ m. The results confirm that TINA is suitable for high-throughput experiments and efficient analysis of biological IN in laboratory and field samples.

2-12 Chromatographic Separation and Wet Oxidation of Oxalic Acid from Aerosols for Radiocarbon Source Apportionment

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Radiocarbon analysis is a powerful technique for the apportionment of fossil and non-fossil sources of carbonaceous aerosols. This technique can be applied to total carbon, organic carbon and elemental carbon, as well as more specific fractions of aerosols. We aim at compound-specific radiocarbon analyses (CSRA) of dicarboxylic acids (DCAs) using a one-step chromatographic separation followed by a chemical wet oxidation and subsequent radiocarbon measurement with an accelerator mass spectrometer (AMS).

DCAs have received much attention because of their role as cloud condensation nuclei and are found in urban, rural, and marine sites. This raises questions about their sources, precursors, and formation processes. Gaseous precursors can react in the atmosphere forming secondary organic aerosols (SOA). Both primary organic aerosols (POA) and SOA can undergo aging processes, from which low-molecular-weight DCAs are produced. The dominant DCAs in aerosols are by a large margin oxalic acid, followed by malonic and succinic acid. Previously, the sources of formic, acetic, and oxalic acid in aerosols were investigated using stable carbon isotopes (Fisseha et al., 2009). In contrast, owing to their low prevalence, radiocarbon measurements of DCAs are seldom conducted. Fahrni et al. (2010) performed CSRA of DCAs using a two-step chromatographic separation. There, water-soluble organic compounds were separated by ion chromatography (IC), followed by high-performance liquid chromatography (HPLC). The fractions were collected, water removed on a vacuum line, and the compounds oxidised to CO2at 950°C with cupric oxide in a quartz glass tube for AMS measurement.

In this work, chemical wet oxidation (Lang et al., 2016) was used to oxidise oxalic acid directly after IC separation without a second chromatographic separation and an additional concentration step. Wet oxidation directly forms CO2from carbonaceous compounds in the eluate whereas inorganic compounds such as sulphates remain unaffected. This simplifies the procedure while achieving lower blanks by omitting additional concentration and separation steps. We focus on the apportionment of fossil and non-fossil sourcesof oxalic acid extracted from filters sampled at urban and rural sites. As a consequence of their low content, pooled fractions of malonic and succinic acid will be measured additionally.

Fahrni et al., Radiocarbon 52, 752-760 (2010)

Fisseha et al., Atmos. Environ. 43, 431-437 (2009)

Lang et al., Radiocarbon 58, 1-11 (2016)

1.3 Source characterization and source apportionment

3-1 Sources of Carbonaceous Aerosols in Urban and Rural Ireland

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A seven-wavelength aethalometer (Magee Scientific, model AE 33) has been deployed in the first detailed study of Black and Brown Carbon aerosols at urban and rural locations in Ireland. Wintertime measurement campaigns were conducted in three small rural towns, with high reported solid fuel (coal, peat and wood) usage for domestic heating. Black Carbon (BC) concentrations determined using the aethalometer correlated closely with EC and OC concentrations, measured using the Sunset OCEC instrument. The BC measurements show a clear diel variation, which was similar at each site: a slight rise between 7:00 - 10:00 followed by a significantly larger peak between 18:00 and 20:00. BC mass concentrations were then attributed to solid fuel burning (BCSF) and traffic (BCTr) using the latest version of the aethalometer source apportionment model (Zotter *et al.* 2017). These results show that solid fuel burning is the dominant source of BC at each of these rural locations. Further online measurements of chemical composition made using a single particle mass spectrometer (ATOFMS, TSI 3800 series) enabled the contribution of each solid fuel type (coal, peat and wood) to be estimated and also provided valuable information on the mixing state of the carbonaceous particles.

In addition to these rural campaigns, measurements have also been made at two locations in Dublin: one background site and one roadside site. A strong seasonal variation in BC was observed at the background location, with significantly higher levels detected during the winter months attributable to residential solid fuel burning. In contrast, vehicular traffic was the dominant source of BC at this site during summer months. Measurements from the roadside location in Dublin show large spikes in BC during traffic times, and almost all BC at this site is attributed to vehicular traffic.

3-2 Chemical and optical characterisation of winter rural aerosol

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Carbonaceous aerosol accounts for a considerable fraction of PM10 in Europe. The particles affect the atmospheric radiative balance primarily by their wavelength dependent absorption but also pose a threat to human health. The wavelength dependency of light absorption has not only climatic importance, it can also serve real time measurable information about source apportionment and air quality too. In our study the optical absorption spectra and chemical composition of winter rural carbonaceous aerosol were investigated as part of the EMEP/ACTRIS measurement campaign (01.12.2017-28.02.2018).

Continuous measurement of absorption spectra was carried out with a seven-wavelength aethalometer (AE42, Magee Scientific). In order to increase the reliability of the measured data posterior data treatment was made by using the Weingartner correction scheme. The wavelength dependency of the absorption spectra was quantified by the Aerosol Angström Exponent (AAE). For the chemical analysis 24-hour samples were collected on quartz filters with a Partisol sampler (1 m3 h-1). In order to follow the diurnal variation of the chemical composition 6-hour Hi-Vol filter samples were also collected for 2 weeks. PM10 concentration was monitored with a Thermo FH62C14 instrument working on the beta attenuation principle. The concentration of EC and OC was measured on 6-hour base by using a Sunset Laboratory Model 4G EC/OC analyzer. Levoglucosan characteristic for wood burning was quantified by GC-MS while polycyclic aromatic hydrocarbons were analyzed by using HPLC with fluorescence detection. Both anhydrosugars and diagnostic pairs of PAHs were used to estimate the contribution of wood burning to PM10 concentration.

We observed that the absorption spectra can be more precisely quantified using wavelength range specific AAE than the widely used wavelength independent one. We identified two characteristic wavelength regions. One is related to the UV-Visible spectral region (370nm-520nm), while the other refers to the Visible-Near IR wavelength range (520nm-950nm). Based on the deduced data we demonstrate also here the site specific diurnal cycle of AAE370-520nm and AAE520-950nm and its relation to wavelength independent AAE data (AAE370-950nm). Levoglucosan accounted for 9% and 3% of TC and PM10 mass concentration, respectively, indicating the considerable contribution of wood burning to carbonaceous aerosol and PM10 at the site. The correlation between the absorption and chemical properties of carbonaceous aerosol in daily as well as 6-hour samples will be shown in the presentation.

Acknowledgement: This work was supported by the ACTRIS-2 project (EU's Horizon 2020, No 654109), the GINOP-2.3.2-15-2016-00036 and by the European Union, co-financed by the European Social Fund under project number EFOP-3.6.1-16-2016-00014 and by the János Bolyai Research Scholarship of the HAS. The technical assistance by Katalin Galló Békefi is also gratefully acknowledged.

3-3 Long-term trend of black carbon (BC) from fossil fuel combustion and wood burning emissions in Switzerland

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Black carbon (BC), the light absorbing part of atmospheric particulate matter (PM), is of strong importance for the radiative forcing of the atmosphere. In addition, BC is a serious air pollutant as exposure to BC has adverse impacts on human health. Atmospheric BC mainly originates from fossil fuel (FF) combustion and wood burning (WB) emissions. The influence of other sources of BC is negligible in Switzerland, and in large parts of Europe and the world.

A source apportionment method for BC based on the measurement of light absorption of PM at multiple wavelengths has evolved in the past years and is nowadays widely used [1]. This method relies on the stronger absorption of wood burning related BC in the blue and near ultraviolet wavelength region and allows the calculation of the contributions from FF combustion and WB emissions to total BC. We applied this method to long-term measurements of the light absorption of PM2.5 as performed since 2008 at various locations in Switzerland representing different site types. The calculated contributions from FF combustion and WB were tested for plausibility by using auxiliary data such as measurements of levoglucosan, NOx and PAHs. It was found that total BC as well as BC from FF combustion is significantly declining (95% confidence level) at all sites. In contrast, the contribution from wood burning emissions remained constant during the past years. The improvement in total BC is thus entirely due to declining contributions from fossil fuel combustion, i.e. mainly from road traffic and other diesel engines. Our findings illustrate a remarkable success of the measures taken to reduce black carbon emissions from diesel engines, in particular the introduction of diesel particle filters. In contrast, little progress has been made to reduce black carbon emissions from wood burning appliances. As a consequence, the contribution from wood burning emissions to BC has surpassed the contribution from fossil fuel combustion in non-urban and non-traffic related environments.

[1] Zotter, P., H. Herich, M. Gysel, I. El-Haddad, Y. Zhang, G. Močnik, C. Hüglin, U. Baltensperger, S. Szidat and A. S. H. Prévôt (2017). *Atmos. Chem. Phys.*, 17, 4229–4249.

3-4 PAH emission patterns from different domestic firewood combustion devices

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Emissions from residential wood combustion contribute significantly to the overall particulate matter (PM) generation in Austria as well as in Europe. Here we focus on carbonaceous compounds including polycyclic aromatic hydrocarbons (PAHs) in PM originating from small-scale heating devices. PAHs are produced during incomplete combustion processes or pyrolysis of organic material and are emitted as complex mixtures containing structural isomers and derivates. As they undergo long-range transport PAHs can be found in urban as well as rural areas.

This work presents emission patterns of PAH concentrations of different small scale domestic firewood combustion devices containing the 16 US EPA priority PAHs (aPAH16). The combustion devices were operated representing real life operation. TSP measurements were performed in the hot and cooled flue gas. TSP emission samples were collected before and after training the users to optimize firing conditions. Here we present first results of six firewood combustion appliances, all of them operated in a rural area in Styria, Austria. For every heating device, two or three consecutive batches were evaluated according to the users habit. Besides PAHs, major contributors to the chemical composition of TSP were characterized using different analytical methods, i.e. the carbonaceous fraction, anhydrosugars, inorganic ions, humic-like substances. Total PAH emissions decrease after user training and also a shift in PAH patterns can be observed. PAH concentrations determined within the hot or the cooled flue gas reflect the known partitioning of PAHs between the gas and particle phase, driven by their molecular weights. The major PAH amount is quantified in cooled TSP samples, i.e. in the cold flue gas / after dilution. Samples taken from the hot-phase mainly consist of PAHs with higher molecular weights (MW), i.e. MW starting with 228. PAH patterns from cooled-phase samples mainly consist of PAHs with lower molecular weights, i.e. MW starting with 128. Before user training the maximum concentrations of aPAH16 was 4.2 mg/filter, while a maximum concentration of aPAH16 of 0.2 mg/filter was determined after the user training.

Similar to the PAH content, a higher amount of levoglucosan was quantified in cooled-phase samples than in hot-phase samples. Also, a characteristic distribution of EC (elemental carbon) and OC (organic carbon) was observed in these two sample fractions. The major amount of elemental carbon was observed in the hot-phase samples, while the cooled-phase samples primarily consist of organic carbon.

3-5 Source contributions to carbonaceous aerosol after the Beijing coal burning ban - insights from size resolved radiocarbon measurements

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In order to combat bad air quality a coal ban was instituted for the winter 2017/18 in Beijing and other Northern Chinese cities. Although the coal ban was partially lifted in early December 2017, coal combustion likely remained reduced for the rest of the winter compared to previous years.

We collected size-resolved samples in the period from January to March 2018 using a 5-stage high flow impactor (Copley, Model 130) with cut-off sizes of 2.5, 1.4, 0.77, 0.44, 0.25 mm. The particles with diameters < 0.25 mm were collected on a back-up filter. Radiocarbon analysis of the impactor deposits allowed us to unambiguously apportion fossil versus non-fossil sources of organic carbon (OC), elemental carbon (EC), water-soluble, and water-insoluble OC (WSOC and WIOC). Three 24-hr impactor samples of polluted periods and one composite sample of three clean periods were analyzed.

In the winter 2018, fossil source contributions were close to 70% for EC and 50% for OC, and did not differ strongly between polluted and clean periods. The fossil source contribution to WSOC is roughly the same as for WIOC. Considering that fossil fuel sources emit only small amounts of primary WSOC, this highlights the importance of secondary aerosol formation from fossil sources in Beijing. The source contributions to EC show a distinct size dependence, with the highest fossil contribution to particles in the smallest size range (<0.25 mm) and in the largest size range (1.44-2.5 mm). This size dependence is more pronounced in strongly polluted than in clean periods. In contrast, the contribution of fossil sources to all OC fractions does not show a similar size dependence, indicating that primary sources play a minor role for OC.

A comparison with 14C - source apportionment of PM2.5 samples in the winter 2016/17 shows that contributions of fossil sources to both OC and EC were significantly reduced in 2018, likely due to reduced coal combustion. The 14C results will be combined with organic aerosol source apportionment from an Aerosol Chemical Speciation Monitor (ACSM) to further explore the effects of the coal ban on the source contribution to both primary and secondary organic aerosol

3-6 High time resolution measurement and source apportionment of TC, BC and OC, EC

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Measurements of carbonaceous aerosols are of vital importance for local, regional and global air quality monitoring, regional and global climate change investigations. The carbonaceous fractions are frequently separated into organic carbon (OC) and elemental carbon (EC) based on their volatility using thermal-optical methods. While the results for OC and especially EC concentrations vary significantly for different thermal evolution protocols, the total carbon (TC) concentration is very consistent between methods (Karanasiou et al., 2015). Therefore, we show an equivalent method and a new and innovative instrument, capable of highly time resolved measurement of total carbon (TC), which, combined with black carbon (BC) measurements (Drinovec et al., 2014; Hansen et al., 1982), provides an equivalent of OC and EC. We call this approach TC-BC.

"TC-BC" online method combines an optical method for measuring BC by the Aethalometer AE33, and a thermal method for TC determination by the Total Carbon Analyzer TCA08 is used for source apportionment of carbonaceous aerosols with high time resolution at several measuring sites around the world. TC-BC method determines equivalent organic carbon fraction of carbonaceous aerosols as

 $eOC = TC - b \cdot BC$,

where $b \cdot BC$ is equivalent to elemental carbon (EC). The determined proportionality parameter b is region/site specific and depends to a large extent on a thermal protocol used to determine the EC fraction with the conventional OC/EC method.

TCA08 measures concentration of TC by a rapid combustion of carbonaceous matter (CM) collected on a quartz filter. Pulse of CO2 which is created during combustion phase of the analysis is detected as a large transient increase above the CO2 level in the ambient air used as the carrier gas. Simplicity of the analysis allow us to have high time resolution measurement and easier field deployment of the instrument as no high purity gases are needed.

TC-BC method was validated by comparing averaged high time resolved data to the conventional OC/EC analysis on 24h filters using different thermal protocols (EUSAAR2, IMPROVE, NIOSH) in the winter campaigns in Europe, Asia and N. America: Ljubljana (Slovenia), urban background site; Loški Potok (Slovenia), rural; Ispra/Milano (Italy), urban background, Paris (France), urban background; London (United Kingdom), urban background; Zurich (Switzerland), urban background; Magadino (Switzerland), rural; Beijing (China), urban; New Delhi (India), urban; Los Angeles (United States of America), urban; Additionally, at some sites parallel measurements with aerosol mass spectrometry (AMS or ACSM) allowed us to obtain hourly comparison of OM (AMS) to OC (TC-BC) and determine the OM/OC ratio.

3-7 Emission factors and chemical composition of laboratorygenerated fresh and aged biomass burning aerosols

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Biomass burning (BB) emissions and their atmospheric oxidation products have significant impact on air quality and human health. BB aerosols also influence the global climate by scattering and absorbing light. BB aerosols are composed mainly of organic compounds and elemental carbon. Very little is still known about the chemical composition of BB organic aerosols (BBOA), how it differs among different biomass fuels, and how it is chemically transformed during its oxidation in the atmosphere. In this presentation, we will discuss the main findings of a laboratory BB study aimed at comprehensive optical, physical, and chemical characterization of both fresh and aged BB emissions. Several globally- and regionally-important biomass fuels, such as Siberian, Florida, and Malaysian peats, mixed forest, and mixed grass and brush fuels from the Western USA, were tested in this study. Aerodyne Oxidation Flow Reactor (OFR) was used to mimic atmospheric oxidation processes. The OFR was characterized in terms of OH production rate, particle transmission efficiency, and characteristic lifetimes of condensable compounds. Fresh and aged BBOA were collected using Teflon-impregnated glass fiber (TIGF) filters followed by XAD cartridges to capture gas-phase semi-volatile organic compounds. Extracts were then analyzed using gas chromatography - mass spectrometry for polycyclic aromatic hydrocarbons (PAH), alkanes, and polar compounds. Over 200 individual compounds were identified and quantified in this study. We will report emission factors for organic compounds, particulate matter, carbon monoxide, and nitrogen oxides. The effect of atmospheric aging on chemical composition and aerosol optical properties will also be discussed.
3-8 Impact of alternative jet fuels on aircraft particle emissions in cruise

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We present results from the ECLIF/ND-MAX flight campaigns which aimed to characterize the effects of alternative jet fuels and clean-burning engines on the emissions of jet engines in cruise. Funded by DLR and NASA the project utilized the DLR Falcon20 and the NASA DC-8 research aircraft quipped with a variety of trace gas, aerosol and ice particle instruments to characterize the emissions of the DLR A320 Advanced Technology Research Aircraft (ATRA) in cruise as it burned mixtures of different alternative jet fuels with conventional, well analyzed Jet A-1 fuels. During formation flights performed with the DC-8 over northern Germany in January and February 2018 the aerosol and trace gas properties in hundreds of plume crossings at different altitudes, meteorological conditions and engine states were analyzed. During a mission in fall 2015 utilizing the DLR Falcon 20 also data in the near field behind the engine exhausts were taken. In addition, flights in the contrails of commercial A320-class aircraft were performed to sample emissions from a new generation of low-emission, lean-burning jet engines. The analysis presented here is focused on investigating the effects of fuel and engine technology on soot emissions.

3-9 Potential contribution of animal faeces to resuspended PM1-10 in urban environment

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The respirable fraction of resuspended urban road dust may contain potentially hazardous pollutants which may cause adverse health effects leading to an increased risk of respiratory illnesses. Phosphorous was found in resuspended road dust in significant concentrations part of which might originate from birds' faeces. Specific biomarkers such as faecal sterols and bile acids are frequently used to verify the presence of faecal pollution in various environmental samples. The quantification of the contribution of faecal materials is usually based on the analysis of bile acids. These persistent and refractory organic compounds are ubiquitous tracers since they are found in digestive systems of all mammals and birds and not much dependent on diet. In this study, by measuring the concentrations of bile acids from the extracts of resuspended PM1-10 samples collected from paved roads on urban locations we estimated the potential mass contribution of birds' faeces to the respirable fraction of road dust. A special sampling unit was applied for the collection of resuspended and respirable road dust in Veszprém and Budapest, Hungary. The phosphorous concentrations of samples were measured by particle induced X-ray emission (PIXE), and bile acids concentrations were determined by gas chromatography-mass spectrometry (GC-MS). Phosphorous was found in the resuspended PM1-10 fraction in concentrations of 1-2 mg g-1 whereas bile acids such as LCA (lithocholic acid), DCA (deoxycholic acid), CDCA (chenodeoxycholic acids) and HDCA (hyodeoxycholic acid) were identified in total concentrations of 5-10 µg g-1. Our results indicate that wind- or traffic-driven resuspension of dry animals' faeces that has never been considered previously as a potential source of urban PM1-10, may be a detectable contributor to urban PM1-10 with all its potential health and epidemiological implications.

The authors are grateful for the financial support of the GINOP-2.3.2-15-2016-00055 Project through the National Research, Development and Innovation Office, Hungary. This paper was supported by the János Bolyai Research Scholarship of the Hungarian Academy of Sciences.

3-10 Spring aerosol in urban atmosphere: analytical and statistical assessment for source impacts

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High density of population and multi-profile activities in megacities objectively lead to large-scale ecological impact emphasizing the need to assess the sources of air pollution. Spring is the season when complementary impacts of agriculture fires/biomass burning are increasing significantly in accordance to biogenic activity which can be observed at the same time. In the complex situation of the plurality of anthropogenic emissions, an important research task remains for the megacity environment to identify the contributions of the major sources including biomass burning and biogenic, through aerosol composition analyses.

This study reports the evaluation of the air quality in the urban background of Moscow megacity in spring 2017. This period was characterized by significant changes of air temperature, mass advection, and solar radiation. Synergistic coupling of PM10 mass concentration, light absorbing properties, aerosol composition and meteorological measurements has been performed in urban background at the Meteorological Observatory of the Moscow State University (MSU).

Organic and elemental carbon (OC, EC) as well as 76 organic compounds like alkanes, polycyclic aromatic hydrocarbons (PAHs), oxidized PAHs (o-PAHs), hopans and anhydrosugars, polyols, primary- and secondary saccharides were quantified to describe the carbonaceous particle fraction. Thirteen ions characterize the inorganic composition. Angstrom Absorption Exponent (AAE) parametrization estimates the relative contributions of agriculture fires and domestic biomass burning around the city to urban aerosol composition dominated by fossil fuel combustion.

Combining attentive analytical chemical and statistical approaches, representative chemical compounds are able to describe the highest quantity of variability, evaluated together with the highest analytical validity of the chemical compounds. Comprehensive principal component analyses (PCA) supported by chemical markers, meteorological parameters and air mass transportation analyses is able to highlight the emission sources from fossil fuel combustion, heavy-duty transport, air mass transportation from agriculture fires and domestic activity. Secondary organic and inorganic aerosol formation and photochemical processes occur in the period of increasing biogenic activity.

3-11 Incorporating Hopane Degradation into Chemical Mass Balance Source Apportionment of PM2.5

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Hopanes are useful molecular markers for tracking airborne fine particulate matter (PM2.5) associated with vehicular exhaust in receptor models. However, they undergo atmospheric degradation. This causes deviations from the underlying assumption of mass conservation in receptor models and leads to biased estimation for source contributions. Little work has been conducted to account for this issue in receptor modelling. In this study, we analyzed the PM2.5 chemical speciation data including C27–C31 hopanes from two urban sites in the Pearl River Delta region, China. We developed an approach using ambient-to-source ratio of hopane homologues to show evidence of hopane degradation. Organic carbon (OC) and PM2.5 were then apportioned using the chemical mass balance (CMB) model, with the emphasis on considering hopane degradation. We applied a set of volatility-dependent degradation factors to correct for the loss, and determined the extent of degradation through identifying the statistically optimal CMB solution. The results reveal that neglecting hopane degradation would underestimate the primary vehicular OC and PM2.5 contributions by ~55% in warm season and by 35% in cold season. The method developed in this work could be used to improve accuracy of vehicular source contribution estimation in other urban locations.

1.4 Aerosol concentrations, trends andtransport – measurements and models

4-1 Pre-industrial to industrial changes of carbonaceous particles (OC, EC/BC) from glacier ice cores

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The impact of aerosol particles on the Earth's radiation balance remains poorly constrained, leading to considerable uncertainties in predicting the climate sensitivity to changing levels of greenhouse gases. A large part of these uncertainties is related to the deficient knowledge of the magnitude of pre-industrial emissions, particularly for carbonaceous compounds forming a major fraction of the atmospheric aerosol. For modelling the aerosol forcing, emission estimates are used, which are often highly uncertain particularly for pre-industrial times. A different approach is to determine the pre-industrial aerosol concentration and composition from analysis of aerosol related chemical compounds in ice cores. Here we present pre-industrial to industrial concentration changes of carbonaceous particles from Alpine glacier ice cores with a focus on water-insoluble organic carbon (WIOC) and elemental carbon (EC) separated into fossil and non-fossil contribution using the 14C content (radiocarbon based source apportionment) as well as black carbon (BC). The preindustrial to industrial record of 14C in WIOC and EC indicates that fossil and non-fossil concentrations of these two carbonaceous aerosol fractions show characteristic differences in their temporal variation, demonstrating separation into their fossil and non-fossil component to be crucial for a quantitative reconstruction of emissions. WIOC shows a strong increasing trend between 1940 and 1980, mostly of non-fossil origin. This is not reflected in the European emission estimates with a mismatch of up to a factor of five, revealing that bottom-up emission inventories may heavily underestimate the atmospheric OC loading, thus limiting the current capacity of models in estimating aerosol forcing. EC has highest values in the first half of the 20th century, to a large extent caused by fossil fuel emissions. An independent BC record from another Alpine ice core supports this finding and in a short excursion will be presented to discuss the impact of industrial BC emergence on the 19th century glacier retreat in the Alps.

4-2 15 year long-term trend of OC and EC in PM at Melpitz site in Germany using an inter-comparison of thermographic and thermo-optical data

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Organic (OC) and elemental carbon (EC), sum total carbon (TC), were quantified on daily quartzfibre filters (HV samples PM10, PM2.5 and PM1, DIGITEL DHA-80) at the TROPOS site in Melpitz (German lowlands in Central Europe, 12°56'E, 51°32'N, 86 m a.s.l.) Melpitz represents the regional background in Central Europe (Spindler et al. 2012 and 2013) and highest EC concentrations were found during air-masse transport from East especially in winter (van Pinxteren et al. 2016). The concentrations in 2013 for OC und EC were 3.12 and 2.08 µgm-3. The quantified amount of OC or EC depends strongly from the method and the temperature protocol used. From 2003 up to 2014 a two-step thermographic method (TGVDI) following a variation of VDI2465 (Part 2) was realized. Because this method doesn't exceed 650°C, also impactor samples on aluminum foils can be analyzed. Charring processes cannot be accounted here (Spindler et al 2012). Therefore 2012 a thermo-optical method (TO) using the Lab OC-EC Aerosol Analyzer (Sunset Laboratory Inc.) together with the temperature protocol EUSAAR2 (Cavalli et. al 2009) was introduced. Charring correction is done by Transmittance (TOTEUSAAR2). In European networks, EMEP1), ACTRIS and ACTRIS22) this method is the preferred technique. Both methods were used for three years (2012-14) in parallel. For the transformation of TOTEUSAAR2-results from 2015 to 2018 back to quasi TGVDI-results linear conversion equations for OC, EC and TC were derived from daily measurements (Equation 1).

[OC; EC; TC]TGVDI = m x [OC; EC; TC]TOTEUSAAR2 + n(1)

Because there was no dependence from the particle size but from the season, conversion equations were calculated for the twelve months of the year over all three sizes as a three year mean (intercomparison). For OC the factors m for February and May are in the range of 0.794 and 0.601 respectively. Using this factors continuous falling long-term trends (2003-2018) for OC (- $0.036 \mu gm$ -3a-1) and EC (- $0.073 \mu gm$ -3a-1) could be reconstructed quasi without inhomogeneity. A recalculation of OC and EC detected by different thermographic and thermo-optical analyzing methods is impossible mostly, because it strongly depends from the place of measurement, the meteorological conditions and the chemical character of carbonaceous aerosol detected.

Cavalli et al. (2010) Atmos. Meas. Tech., 3. 79-89.

Spindler et al. (2012) J. Atmos. Chem. 69, 127-157.

Spindler et al (2013) J. Atmos. Chem. 70, 165-195.

Van Pinxteren et al. (2016) Faraday Discuss. 189, 291-315.

1) Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe

2) Aerosols, Clouds, and Trace gases Research InfraStructure network

4-3 Black Carbon in Saharan and Arabian Dust Layers during A-LIFE

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The A-LIFE (Absorbing aerosol layers in a changing climate: aging, lifetime and dynamics) field experiment in Cyprus in 2017 investigated absorbing aerosol layers containing mixtures of dust and pollution and their interaction with the atmosphere over the eastern Mediterranean with ground-based and airborne instrumentation. With its strong absorption potential, black carbon contributes to warming of the atmosphere. Mixed into dust layers, black carbon can enhance light absorption and therefore influence the optical properties of the dust layers. In this study here, the focus is on mass concentration, size distribution, and mixing state of refractory black carbon (rBC) measured with a Single Particle Soot Photometer (SP2) on board of the DLR research aircraft Falcon during A-LIFE. The Falcon was further equipped with a range of in-situ aerosol instruments to study particle concentration, size, and composition, and a lidar for remote sensing.

High concentrations of rBC mass were found in the dust layers over the Mediterranean, in some cases exceeding 500 ng/m³, particularly in dust layers originating from the Arabian peninsula. Dust layers originating from the Saharan desert exhibited a large variability in rBC particle properties, with mass concentrations ranging from 20 to over 300 ng/m³. This variability is mainly connected to different levels of pollution, with less polluted dust layers at higher altitudes. Arabian dust layers were encountered below 4 km altitude, while Saharan dust layers were detected up to 10 km altitude. Highest rBC mass concentrations were measured in dust layers at lower altitudes, where particles were also larger, with mass median diameters of the rBC mass size distribution up to 250 nm. Properties of rBC particles in many of the investigated dust layers are more similar to pollution layers with larger rBC particles with less coating than to clean tropospheric background.

4-4 Properties of black carbon particles in biomass burning plumes

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During two HALO aircraft campaigns, the microphysical and cloud-nucleating properties of biomass burning aerosol from Brazil and the African continent was measured with an identical measurement setup, using a Single Particle Soot Photometer (SP2, Droplet Measurement Technologies) and a Cloud Condensation Nuclei Counter (CCNC, Droplet Measurement Technologies). Additionally, a home-made single stage impactor was used for collecting aerosol samples (100 nm lower cut-off) for micro-spectroscopy analysis. This combination of online and offline measurement techniques offers the unique opportunity to study particle hygroscopicity, morphology, black carbon (BC) content and size distribution, as well as the elemental composition of BB aerosol in more detail.

In September 2014, the ACRIDICON-CHUVA campaign was performed over the Amazon basin sampling aerosol, BC and CCN concentrations during the burning season[1]. During the campaign, we observed a pronounced gradient in regional BC concentrations, typically increasing from the northwestern (more pristine) to the southeastern (more influenced by fresh regional fires) regions of the basin. Moreover, most of the BC from regional fires was found to be confined to the lower 4 km of the atmosphere (concentrations > 1 μ g m-3), decreasing to only a few nanograms per cubic meter in the upper troposphere, with the exception of some outflow regions. In addition to the local vegetation fires, we found that BC-rich pollution from African BB can be deeply advected into the Amazonian atmosphere after being transported for several days over the South Atlantic Ocean. The

4-5 Black carbon particles in the northern hemispheric lowermost stratosphere

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In a recently published PNAS article (Ditas et. al, 2018) we demonstrate the impact of wildfires on the abundance and aging of black carbon in the lowermost stratosphere (LMS) measured between Europe and the US. Although these particles underwent a long-range transport in high altitudes at about 10 - 12 km, their influence on the atmosphere is limited by dry- and wet-scavenging. Therefore, in this follow up study we aim to address following questions:

 \cdot How effective is the longitudinal transport of Canadian biomass burning emissions in the northern hemisphere?

• To which degree do wildfires in Siberia influence BC particle properties in the LMS?

Until now, there is no global characterization of black carbon particles in the upper troposphere and lowermost stratosphere. Our new study will deal with 45 IAGOS-CARIBIC flights between the US (Munich ↔ San Francisco, Mexico City, and Los Angeles) and Asia (Munich ↔ Tokyo, Beijing, Hong Kong and Shanghai). The data, measured with a modified SP2 instrument located in the instrumented airfreight container on board a Lufthansa passenger aircraft, shows clear differences in black carbon mass concentrations, core diameter and coating thickness above the Atlantic Ocean and the Asian continent. Based on different case studies (including related flights in both directions), we found a decreasing influence of Canadian wildfires on the amount of black carbon in the LMS towards the east. Especially, over Europe there seems to be a sink of these large and thickly coated biomass burning black carbon aerosol particles. However, does this mean that lowpressure systems are responsible for the wet-scavenging of these biomass burning emissions? Or are these emissions transported towards the pole or more southern regions with a possible dilution with background air? We will try to address these questions with our regular flights and the extensive data set. But anyhow, it seems that the influence of Siberian wildfires on the abundance of black carbon in the LMS is less pronounced compared to the huge impact above the Atlantic Ocean, and globally the abundance and mixing state of black carbon particles in the LMS strongly depend on region and season.

J. Ditas, N. Ma, Y. Zhang, D. Assmann, M. Neumaier, H. Riede, E. Karu, J. Williams, D. Scharffe, Q. Wang, J. Saturno, J. P. Schwarz, J. M. Katich, G. R. McMeeking, A. Zahn, M. Hermann, C. A. M. Brenninkmeijer, M. O. Andreae, U. Pöschl, H. Su, Y. Cheng (2018): Strong impact of wildfires on the abundance and aging of black carbon in the

4-6 Improvement of Black Carbon emissions and modelled concentrations in Germany

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Black carbon (BC) acts as a short-lived greenhouse gas and is associated with enhanced morbidity, respiratory and cardiovascular disease. Thus, reducing BC emissions results in a win-win situation for both climate and health. However, uncertainties in BC emissions are still quite large. We provide a comparison between two detailed emission inventories for Germany: CAMS and GRETA. Differences in the BC inventories are found because of differences in PM emission factors for specific source sectors and differences in used BC fractions in PM composition splits that speciate the total reported PM into species. These are related to assumptions within each emission sector. The focus was on the residential heating sector (stoves) and the transport sector (e.g. diesel exhaust), which are the sectors that contribute most to BC. Differences were addressed based on literature reviews and a new consistent BC emission inventory was created.

Baseline GRETA emissions and the new emission set were used in the regional-scale LOTOS-EUROS chemistry-transport model to calculate BC ambient air concentrations over Germany. The emissions in the model were labeled per source sector and region, so that the contribution of a specifc source (area) on the total concentration can be investiated efficiently. Modelled concentrations were compared with observations of ambient BC concentrations from filter analysis and aethalometer data. Different types of locations (different regions, urban/rural) were used to evaluate the different aspects of the emission changes in detail. In this way the update of the emission inventory can be evaluated and directions for further refinement of the inventory can be derived.

4-7 Occurrence of PAHs and new tracer of polyethylene plastic combustion, 1,3,5-triphenylbenzene in PM10 collected in residential area of Krakow agglomeration, South Poland

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Over the last few decades a concern over the health effects associated with air pollution was growing, mainly due to their carcinogenic and mutagenic properties. Nowadays, many harmful aerosols enter the atmospheric air. Atmospheric aerosols constitute a complex mixture of organic and inorganic compounds and biological materials. The group of the most widespread and particularly dangerous atmospheric pollutants in the present times includes particulate matter (e.g. PM1, PM2.5, PM10). They have sorption properties, and thus, other harmful compounds may be deposited on their surface. The most dangerous of these compounds are polycyclic aromatic hydrocarbons (PAHs).

The aim of the study was determination of chemical composition of atmospheric aerosols collected in Krakow agglomeration (Wadowice) from February 2017 to October 2017. One aspect of research was to fill the gap on the occurrence of tracers of co-combustion of polyethylene plastics in residential boiler. All samples were taken using a low-volume sampler PNS-15 on quartz fibre filters and represent PM10 fraction collected with 24h resolution. The analytical work comprised determinations of PAHs (e.g. anthracene, benzo(a)pyrene, chrysene, naphthalene, pyrene) and 1,3,5-triphenylbenzene (135TPB) by means of gas chromatography-mass spectrometry (GCMS) (Trace 1310 Gas Chromatograph, ITQ 900 Mass Spectrometer, TriPlus RHS Autosampler). The elemental carbon (EC) and organic carbon (OC) were measured with a Sunset Laboratory OCEC Aerosol Analyzer using EUSAAR2 protocol.

Concentration of particulate matter in 2017 ranged from $10,80\mu$ g/m3 in August to $406,80\mu$ g/m3 in January. The highest concentration of PM10 was recorded in the colder months of 2017. The concentrations of PM10 in colder months was much above the daily limit value (50μ g/m3). In the warmer months, concentration of PM10 did not exceed the acceptable standards. The average concentration of OC recorded in colder months of 2017 was 121,98 μ g/m3, while in warmer months was 5,88 μ g/m3. The same relationship was noted for the analysis of concentrations of polycyclic aromatic hydrocarbons. Concentrations of PAHs in March was 8 times higher than in August. The analyses showed an 7 times higher concentration of carcinogenic PAHs in March (70,10ng/m3) than in August (9,42ng/m3). Analyses confirmed the presence of 1,3,5-triphenylbenzene, in whole measuring period, and its average concentration was 0,99ng/m3 and 0,29ng/m3, in March and August, respectively. 135TPB is one of many exhaust gas components caused by burning of polyethylene plastics (mainly plastic bags). It is important to urgently expand the environmental monitoring strategy with new tracers, especially 135TPB. This will allow to get more accurate information on the threat to human health from the presence of air pollutants.

Acknowledgement

This work partially financed by AGH UST Rector Grant No. 95/2017 and AGH University Grant No. 11.11.210.374.

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4-8 Polycyclic aromatic hydrocarbons (PAHs) and their nitrated and oxygenated derivatives in air of the Arabian Basin

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Polycyclic aromatic hydrocarbons (PAHs) as well as their nitrated (NPAHs) and oxygenated (OPAHs) derivatives are formed by incomplete combustion of fossil and biofuels. Accordingly, these substances are emitted e.g. by road and ship traffic, various industries, and biomass burning (Bandowe & Meusel, 2017). Besides these primary sources, NPAHs and OPAHs can be formed in the atmosphere from PAHs in atmospheric oxidation reactions (Finlayson-Pitts & Pitts, 2000). Many NPAHs are more toxic (e.g. carcinogenic) than their parent PAHs (IARC, 2012). In addition, quinones, a major subgroup of OPAHs, have received much attention in recent years, as upon inhalation they are effective precursors for reactive oxygen species (ROS) which can have adverse health effects (Walgraeve et al., 2010). Despite their adverse impact on human health, the atmospheric concentrations of NPAHs and OPAHs, their cycling and fate in the environment are not well studied.

The AQABA (Air Quality and Climate Change in the Arabian Basin) project was a comprehensive ship-borne campaign in summer 2017 measuring a wide range of air pollutants, aerosols, atmospheric oxidants and auxiliary parameters over the Mediterranean Sea and the seas around the Arabian Peninsula. Although the region is populous and public health is compromised by heat extremes, atmospheric dust and air pollution, relevant data and knowledge is limited. For this study, active air samplers were applied when the ship was passing different locations including very clean areas (Arabian Sea), highly polluted areas near the coast (from cities and shipping) and the Arabian Gulf area (petrochemical industries). Phase distribution in the atmosphere was addressed by differential sampling of the gas and particulate phase (PM10, size-segregated).

PAHs and NPAHs in the air samples were extracted with organic solvents and identified/quantified by gas chromatography/mass spectrometry (GC/MS), while heavy metals were determined by inductively coupled plasma mass spectrometry (ICP-MS).

PAHs and OPAHs were found in the 100-1000 pg/m³ range in air over the Red Sea, the Arabian Gulf and the Gulf of Oman. Nitrated PAHs were found in the 1-10 pg/m³ range in air of the entire region. Source regions and less polluted sites could be differentiated based on the concentrations and composition patterns of PAH and NPAHs. Furthermore, plumes could be identified and attributed to their origin. The heavy metal content in the sampled air reflects both crustal dust and anthropogenic pollution events. The spatial variation of pollutants, composition patterns, mass size distributions and sources in the region will be presented and discussed.

4-9 Temperature effect on phase state and reactivity controls atmospheric multiphase chemistry and transport of PAHs

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Polycyclic aromatic hydrocarbons like benzo(a)pyrene (BaP) in atmospheric particulate matter pose a threat to human health because of their high carcinogenicity. In the atmosphere, BaP is mainly degraded through a multiphase reaction with ozone, but the fate and atmospheric transport of BaP are poorly characterized. Earlier modeling studies used reaction rate coefficients determined in laboratory experiments at room temperature, which may overestimate/underestimate degradation rates when applied under atmospheric conditions. Moreover, the effects of diffusion on the particle bulk are not well constrained, leading to large discrepancies between model results and observations. We show how regional and global distributions and transport of BaP can be explained by a new kinetic scheme that provides a realistic description of the temperature and humidity dependence of phase state, diffusivity, and reactivity of BaP-containing particles. Low temperature and humidity can substantially increase the lifetime of BaP and enhance its atmospheric dispersion through both the planetary boundary layer and the free troposphere. The new scheme greatly improves the performance of multiscale models, leading to better agreement with observed BaP concentrations in both source regions and remote regions (Arctic), which cannot be achieved by less-elaborate degradation schemes (deviations by multiple orders of magnitude). Our results highlight the importance of considering temperature and humidity effects on both the phase state of aerosol particles and the chemical reactivity of particulate air pollutants.

Reference:

Mu, Q., Shiraiwa, M., Octaviani, M., Ma, N., Ding, A. J., Su, H., Lammel, G., Poschl, U., and Cheng, Y. F.: Temperature effect on phase state and reactivity controls atmospheric multiphase chemistry and transport of PAHs, Sci. Adv., 4, 8, 10.1126/sciadv.aap7314, 2018.

4-10 Chemical characterization of size-selected carbonaceous particles emitted by internal combustion engines

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On-road motor vehicles are important sources of fine carbonaceous particles, which present acknowledged health and environmental risks. At the same time, there is a critical lack of certification procedures for the smallest particles (<23nm). The development of such measurement procedures requires a deep understanding of the emitted particle characteristics (morphology, structure, chemical composition, volatility, reactivity), and their dependence on size. In the framework of the PEMs4Nano project (H2020), this information will be used to develop an extensive model of soot formation in an internal combustion engine, allowing the development of measurement procedures down to 10nm. This work presents the investigation of the chemical composition of size-selected carbonaceous particles emitted by a gasoline direct injection engine.

Particulate matter studied in this work was produced by a generic single-cylinder engine that can be operated in various working regimes. Particles were sampled using a cascade impactor (NanoMoudi-II, TSI) which allows size-separation of sampled particles into 13 different size bins. The analysis of the chemical composition of size-selected particulates allows us to identify their main production source. Since the main interest of this work is in small particles, only five size bins ranging from 180 to 10 nm were analysed.

The chemical characterisation of the collected particles is performed using a custom-built two-step laser mass spectrometer (L2MS, Faccinetto et al, Environ Sci Technol, 2015). Combining soft (low-fluence) laser desorption and various ionization wavelengths, our instrument is able to provide detailed molecular analysis (with little to no fragmentation) on chemical classes of critical interest such as organosulphates, oxygenated and nitrogenated hydrocarbons, polycyclic aromatic hydrocarbons, and heavy metals. These compounds are useful in determining the sources of PM in the exhaust (e.g. combustion, fuel additives, lubricating oil, mechanical wear, etc). Additional high-resolution chemical mapping is performed using a commercial Secondary Ion Mass Spectrometer (IONTOF).

Principal component analysis (PCA) was used to highlight subtle differences in mass spectra of differently-sized soot particles, denoting variations of their chemical composition (Irimiea et al, RCMS, 2018; Irimiea et al, Carbon, 2019). PCA is able to emphasize differences and similarities in the chemical composition of size-selected particles and also to identify the species that are responsible for that. The latter allows determining the contribution of various sources on different size bins.

The combination of mass spectrometric studies with statistical procedures reveals indisputable evidence of the chemical composition size-dependence. This information represents essential physico-chemical data necessary to develop a reliable portable device for the measurement of ultra-fine carbonaceous particles emitted by automobile engines.

1.5 Bioaerosols

5-1 Potential role of the cloud microbiota in atmospheric chemistry

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Although microorganisms were discovered by Pasteur in the air, the investigation of their activity in the atmospheric compartment is rather recent. Our team works mainly on microorganisms present in clouds1. Cloud samples are collected at the puy de Dôme observatory which is labelled at the international level as a GAW (Global Atmosphere Watch) station.

Our objective is to study the potential role of microorganisms in the chemistry of clouds. We have shown that microorganisms are metabolically active in clouds and can thus potentially modify the chemical composition of clouds and be an alternative route to radical chemistry (particularly photochemistry).

We have mainly studied the biotransformation of simple carbon compounds (acetate, succinate, formate, methanol, formaldehyde) which are the most concentrated compounds in clouds, and the interaction of microorganisms with oxidants (H2O2 and Iron) which are the main sources of radicals 2,3,4.

Using microcosms mimicking the cloud environment (temperature, UV light...) we have determined biodegradation rates and shown that they are within the same range of order than photo-transformation rates. In parallel a metatranscriptomic approach revealed the in situ activity of the cloud microbiote which is completely consistent with in lab biodegradation experiments5. Work is now in progress to introduce this biological activity in cloud chemistry models.

5-2 The microbial Ecology of Aerosols in the East Mediterranean

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Airborne bacteria are ubiquitously found in the atmosphere, with changing concentrations and compositions according to the different air masses, wind intensity, particulate matter (PM) concentration, etc. Airborne bacteria can travel great distances and may affect human health by spreading pathogens; they express proteins that serve as ice nuclei, potentially affecting cloud formation, and could affect agriculture and ecosystems health by spreading pathogens and bacteria that impact biogeochemical cycles. These effects are likely to differ according to the different airborne bacterial community composition. Characterizing the airborne microbiome in air masses from different origins, or that followed different trajectories, could provide valuable data to improve our understanding of global health and environmental impacts.

We present a comparative study on the diversity and composition of airborne bacterial communities, based on dust from various air-masses and several distinct origins that were collected at a single location, in Rehovot, Israel. DNA was extracted from the atmospheric dust samples and used for sequencing a region encoding for the ribosomal small subunit (16S) as a proxy for the taxonomy of the bacteria. The sequencing data was then analyzed to provide information on the communities' structures, similarity and diversity.

To better understand the potential environmental and health impacts of these bacterial communities, we also conducted a metagenomic analysis of these samples, providing us with information on the functional genes and metabolic cycles that characterize each air-mass origin.

This work shows, for the first time, a comprehensive comparison between bacterial communities in dust that arrived in the Eastern Mediterranean from different sources and was sampled at a single location, it also provides an insight into the different metabolic cycles that might be expressed by airborne bacteria from different origins.

5-3 A Newly Developed, Inexpensive Single-Particle Fluorescence Spectrometer: Characterization and Application to Handheld Bioaerosol Analysis

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Within the last several decades, many laser-/light-induced fluorescence (LIF) instruments have become commercially available for bioaerosol analysis. Even so, the majority of widespread identification techniques still rely on complicated analysis, as commercial instruments frequently have trouble classifying beyond broad classes of bioaerosol types (e.g. fungal spores versus pollen), and those that can perform this task are usually very expensive. Pollen-counting, for example, is frequently still accomplished via manual visual microscopy due to the costly nature or low spectral quality of UV-LIF technologies.

Here we discuss a technique we recently introduced to analyze many individual particles collected onto a glass substrate utilizing multiple excitation sources [1]. Our previous characterization work assessed the ability of the instrument to probe relevant biofluorophores within standard particles and several species of pollen used as examples [2]. Four excitation sources (280 nm, 350 nm, 405 nm, and 450 nm) were matched with emission maxima previously shown to be important for a large variety of pollen species [3]. The instrument described here can provide a quick, binary assessment of whether particles are either fluorescent or non-fluorescent, similar to the way certain commercial single-particle UV-LIF instruments are operated. Additionally, the instrument can provide well-resolved fluorescence spectra of individual particles at ca. 2 nm resolution. In preliminary experiments, the instrument was shown to distinguish between pollen species with relatively low uncertainty when employing a clustering algorithm [2]. This technique has demonstrated proof-of-concept ability to supplement the current host of bioaerosol LIF instrumentation at a much lower purchase-cost, while also retaining high fluorescence spectral resolution and the long-range potential to serve as a pollen- or spore-counting instrument.

References:

[1] D. R. Huffman, B. E. Swanson, and J. A. Huffman, "A wavelength-dispersive instrument for characterizing fluorescence and scattering spectra of individual aerosol particles on a substrate," Atmos. Meas. Tech. 9(8), 3987–3998 (2016).

[2] B. E. Swanson and J. A. Huffman, "Development and characterization of an inexpensive singleparticle fluorescence spectrometer for bioaerosol monitoring," Opt Express 26(3), (2018).

[3] C. Pöhlker, J. A. Huffman, and U. Pöschl, "Autofluorescence of atmospheric bioaerosols: Spectral fingerprints and taxonomic trends of pollen," Atmos. Meas. Tech. 6(12), 3369–3392 (2013).

1.6 Carbonaceous CCN and INPs

6-1 Freezing activity and fluorescence measurements of ice nucleating macromolecules from birch trees

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Ice nucleating particles (INPs) are known to trigger freezing in supercooled micro-sized droplets, as present in clouds. Field measurements in clouds detected biological particles in situ with the ability to act as INPs [1]. Further, atmospheric dust particles attribute their high ice nucleation activity often to biological INPs (BINPs) absorbed on their surfaces [2], [3]. Moreover, other studies showed a burst in the concentration of BINPs in aerosols during and after rainfall [4]. Thus, BINPs seem to play an important role in atmospheric processes. However, the detection is still a challenge due to low concentrations in aerosols, complex matrices of biological samples and unknown chemical structures of ice nucleating molecules. Birch pollen, suspended in water, release ice nucleating macromolecules (INMs) active at -18 °C [5]. Beside pollen, also aqueous extracts of woods and leaves from birch trees show freezing activities [6]. This study focusses on the investigation of samples from different parts of birch trees. Determination of the ice nucleation activity was carried out using the Vienna Optical Droplet Crystallisation Analyzer (VODCA) setup. Fluorescence measurements were performed to figure out peak maxima, characteristic for known chemical compounds and correlations between ice nucleation activity and fluorescence intensity. Results indicate a correlation between the concentration of INMs in leaves and fluorescence intensity. Therefore, fluorescence spectroscopy needs to be considered as a potential method to detect INMs in bioaerosols and tissues from living organisms.

References:

1. Pratt, K.A., et al., *In situ detection of biological particles in cloud ice-crystals*. Nature Geoscience, 2009. **2**(6): p. 398-401.

2. F. Conen, C.E.M., J. Leifeld, M. V. Yakutin, C. Alewell, *Biological residues define the ice nucleation properties of soil dust*. Atmospheric Chemistry and Physics, 2011. **11**: p. 9643-9648.

3. O'Sullivan, D., Murray, B. J., Ross, J. F., & Webb, M. E., *The adsorption of fungal ice-nucleating proteins on mineral dusts: A terrestrial reservoir of atmospheric ice-nucleating particles*. Atmospheric Chemistry and Physics, 2016. **16**: p. 7879-7887.

4. Huffman, J.A., et al., *High concentrations of biological aerosol particles and ice nuclei during and after rain.* Atmospheric Chemistry and Physics, 2013. **13**(13): p. 6151-6164.

5. Pummer, B.G., et al., *Suspendable macromolecules are responsible for ice nucleation activity of birch and conifer pollen*. Atmospheric Chemistry and Physics, 2012. **12**(5): p. 2541-2550.

6. Felgitsch, L., et al., *Birch leaves and branches as a source of ice-nucleating macromolecules*. Atmospheric Chemistry and Physics, 2018. **18**(21): p. 16063-16079.

6-2 Impact of subpollen particles on ice nucleation in clouds

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Biological ice-nucleating processes, though being very efficient in nucleating ice, are not considered in numerical weather and climate modells due to their low effectiveness. This low effectiveness is caused by the size and mass of biological ice nuclei (e.g. pollen), since they cannot be transported into altitudes, in which biological ice-nucleating processes can take place in high numbers. This study investigates, whether the bursting of pollen can convert an efficient trigger into an effective one regarding ice nucleation. The smaller subpollen particles (short: SPP), which are released by the bursting process, may be able to reach higher altitudes in larger numbers and therefore be able to trigger biological ice nucleation. To which extend this is to be expected and how these subpollen particles will influence the overall ice nucleation in clouds, is the topic of this model study using the modelling system ICON-ART. Based on the work by Zhou (2014), that shows the relative humidity as the deciding factor for initiating the bursting of pollen, a parameterization is developed, which transforms a fraction of pollen into the smaller subpollen particles and therefore simulates the bursting process. These subpollen particles are used as biological ice nuclei by the heterogeneous nucleation parameterization by Phillips et al. (2013) in the model runs. Our results describe the generation of a new additional (biological) mode in the ice number concentration, which manifests itself at altitudes between 800 m and 4000 m, where the temperatures nearly exclusively allow only biological ice nucleating processes. Furthermore a strong reduction in cloud droplets is observed in these heights, which can be explained by the Wegener-Bergeron-Findeisen-process due to the newly formed ice particles. Therefore a strong influence in the composition of mixed-phase clouds can be observed at these altitudes. An additional effect is present at higher altitudes with lower temperatures, in which mostly nonbiological ice nucleation takes place. Due to the heavy consumption of water caused by the biological ice nucleating processes a reduction in ice number concentration occurs.

6-3 A comprehensive characterization of ice nucleation by three different types of cellulose particles

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This study presents the laboratory results of immersion freezing abilities of cellulose particles. Three types of cellulose samples are used as surrogates of supermicron and submicron ice nucleating plant structural polymers. These samples are micro-crystalline cellulose (MCC), fibrous cellulose (FC) and nano-crystalline cellulose (NCC). Our immersion freezing dataset includes data from various ice nucleation measurement techniques available at many different institutions, including both dry dispersion and aqueous suspension techniques. With these methods, we compared all measurement techniques over a wide T range. Specifically, we inter-compared the geometric surface area-based ice nucleation active surface-site density data derived from our measurements as a function of T, $n_{s,geo}(T)$. Additionally, we also compared the $n_{s,geo}(T)$ values and the freezing spectral slope parameter ($\Delta \log(ns, geo)/\Delta T$) from our measurements to previous literature results. Results show all three cellulose materials are reasonably ice active. The freezing efficiencies of NCC samples agree reasonably well, whereas the diversity for the other two samples spans for ~ 10 °C. Despite given uncertainties within each instrument technique, the overall trend of the ns,geo(T) spectrum traced by the T-binned average of measurements suggest that predominantly supermicron-sized cellulose particles (MCC and FC) generally act as more efficient ice-nucleating particles than NCC with about one order of magnitude higher ns, geo(T).

This is a multi-author study which was funded by the German Science Foundation through the Research Unit FOR 1525 (INUIT). A full list of authors can be found in the ACPD discussion paper of this study:

Hiranuma, N., Adachi, K., Bell, D., Belosi, F., Beydoun, H., Bhaduri, B., Bingemer, H., Budke, C., Clemen, H.-C., Conen, F., Cory, K., Curtius, J., DeMott, P., Eppers, O., Grawe, S., Hartmann, S., Hoffmann, N., Höhler, K., Jantsch, E., Kiselev, A., Koop, T., Kulkarni, G., Mayer, A., Murakami, M., Murray, B., Nicosia, A., Petters, M., Piazza, M., Polen, M., Reicher, N., Rudich, Y., Saito, A., Santachiara, G., Schiebel, T., Schill, G., Schneider, J., Segev, L., Stopelli, E., Sullivan, R., Suski, K., Szakáll, M., Tajiri, T., Taylor, H., Tobo, Y., Weber, D., Wex, H., Whale, T., Whiteside, C., Yamashita, K., Zelenyuk, A., and Möhler, O.: A comprehensive characterization of ice nucleation by three different types of cellulose particles immersed in water: lessons learned and future research directions, Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-933, in review, 2018.

6-4 Cloud processing of soot particles and the effect on ice nucleation in subsequent cloud formation cycles

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Soot influences the Earth's radiation budget by directly absorbing solar radiation but can also contribute to cloud formation by nucleating ice crystals or activating into cloud droplets, thus affecting climate through aerosol-cloud interactions. A quantitative understanding of the aerosol-cloud interactions of soot particles, especially their potential to form cirrus clouds, is a key factor to reduce uncertainties in the estimates of the net radiative forcing of black carbon. The ability of soot particles to form ice crystals depends on the particle morphology and surface composition. Less emphasis has been placed on morphology in the past, motivating our current work focussing on quantifying the morphological properties of soot particles and understanding processes that influence it. The heterogeneous freezing ability of soot at low temperatures is especially important, as aircraft emissions are a direct source of combustion particles in the upper troposphere, where cirrus temperatures prevail.

We test the ice nucleation ability on mobility size-selected aerosol of soot generated from a propane flame Combustion Aerosol Standard Generator (miniCAST, JING AG), using the Horizontal Ice Nucleation Chamber (HINC), a Continuous Flow Thermal Gradient Diffusion Chamber. We focus on the cirrus regime in the temperature range 233 - 218 K. In parallel, we investigate soot particle morphology and how it changes as the soot particles form ice crystals, presenting a systematic investigation of the particle morphology derived from Transmission Electron Microscopy (TEM) images probed before and after the ice nucleation cycle within HINC. Finally, we demonstrate how the ice nucleation abilities of the soot particles change in subsequent cloud formation cycles by coupling two HINC chambers in series. We hypothesize that the change in ice nucleation ability in subsequent cloud cycles is due to morphological changes of the soot particles after the initial ice crystal formation event.

We observe negligible heterogeneous freezing of the unprocessed propane soot particles in the first cloud formation cycle, attributing ice formation to homogeneous freezing conditions. However, our TEM results reveal a compaction of the soot particles upon ice nucleation. When the compacted soot particles are re-exposed to a second ice nucleation cycle within HINC, their ice formation ability is significantly altered resulting in an enhanced ice formation ability with the humidity (with respect to ice) conditions required to trigger ice formation being as much as 15% lower than the first cycle. The results are related to different cloud processing conditions and to the changes in morphology.

6-5 Airborne ice nucleating particles in a combined event of biomass burning and mineral dust storm in Israel

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Ice nucleating particles (INP) in the atmosphere can promote the formation of cold clouds and their microphysical properties, and therefore can affect climate. Biomass burning is an important source of carbonaceous and noncarbonaceous particles that can affect atmospheric chemistry and physics, even at long distances from their source emission. Field and laboratory measurements reported contradicting evidence about their ability to nucleate ice, which varies significantly between different biomass burning events, due to their complex chemistry, or due to the presence of prominent INP types, such as mineral dust. Therefore, the importance of these particles as atmospheric INP, and their possible role in ice cloud formation, are still not well understood or quantified.

We will present results from a field campaign, which was conducted in Israel in the Eastern Mediterranean, a key location that frequently experiences mineral dust from main world deserts: the Sahara and the Arabia deserts. The particles were sampled and size-segregated using the Microorifice Uniform Deposit Impactor (MOUDI), and freezing analysis examined the immersion freezing ability of the collected particles, using the WeIzmann Supercooled Droplet Observation on Microarray (WISDOM). Here we will present a characterization of the local INP concentrations and ice nucleation abilities of airborne particles during mineral dust storms, with diverse sources and atmospheric transport paths. We will focus on a case, where a biomass burning event occurred prior to, and during the sampling period, and will show how the chemical, morphological, and freezing properties of the particles have changed at the different size-classes. The results suggest that during biomass burning events, the aerosol population, especially in the lower size ranges, was affeted by the biomass burning particles and the ice nucleation was suppressed.

6-6 Closure study between observed and predicted activation of black carbon containing particles to droplets in fog and clouds

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Black carbon (BC) is a main component of carbonaceous particulate matter, mainly emitted from anthropogenic sources and it is the strongest light-absorber across the full visible range, therefore causing substantial climate warming through aerosol-radiation interactions (ARI). Freshly emitted BC is often externally mixed, which makes it a poor cloud condensation nuclei (CCN) due to its insolubility. BC particles can acquire coatings during atmospheric aging, thereby making them better CCN. This affects the ARI of BC, as increasing its wet removal efficiency reduces total atmospheric BC burden. In this study we address the activation of BC to form droplets in ambient fog and clouds, and assess whether BC activation can be predicted from measured BC properties.

Field experiments were conducted at an urban site, where fog regularly occurs and where a mixture of fresh and aged BC was encountered, and at a high-alpine site frequently exposed to clouds formed on highly aged free tropospheric aerosol. Aerosol was sampled with different inlets during fog/cloud periods to characterize i) exclusively interstitial particles and ii) the aerosol as a whole (interstitial plus droplet residual particles). This makes it possible to compare the properties of particles that activated to cloud droplets with those remaining interstitial, e.g. size distribution (mobility particle size spectrometer) as well as BC core size distribution and mixing state (single particle soot photometer, SP2).

The size distribution data provide the activation cut-off diameter representative of BC-free particles, from which the fog/cloud peak supersaturation is inferred. The SP2 provides the volume equivalent total particle and BC core diameters of BC-containing particles. SP2 data combined with coating hygroscopicity was used as input for κ -Köhler theory to infer the predicted critical supersaturation for CCN activation of BC on a single particle basis.

In fog with very low peak supersaturation, BC particle activation agreed with predictions both qualitatively and quantitatively: activated fraction increased with increasing coating thickness for a fixed core size, the coating thickness at 50% activation decreased with increasing core size, and the observed dependence of the activation cut-off on size and mixing state matched theoretical predictions. Similar agreement between prediction and measurements was also found for the clouds at Jungfraujoch, though with more limited "data coverage" as higher peak supersaturations shift the activation cut-off diameters towards the lower limits of detection of the SP2. In conclusion, assuming spherical core-shell morphology, which is implicitly done in both SP2 data analysis and κ -Köhler theory, describes activation behavior of atmospheric BC in good approximation. This validates application of κ -Köhler theory based on droplet activation in model simulations in which BC size and mixing state are available on a mass or volume basis.

1.7 Optical properties of carbonaceous aerosols, radiative forcing and climate

7-1 Mixing state and hygroscopicity of black carbon aerosol in severe haze in the North China Plain

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Black carbon (BC) is the most strongly light-absorbing species in atmospheric aerosol. Recent studies found that BC-containing particles may modify the structure of planetary boundary layer and thus enhance haze pollution, especially in densely populated areas, for instance, in China. It is however difficult to quantify this effect due to their complex mixing state, hygroscopicity and the high spatial variability in concentration. During an intensive field campaign conducted in a cold season in the North China Plain, the mass size distribution and mixing state of BC aerosols was measured with a single particle soot photometer (SP2). During a severe haze event, the BC mass concentration exceeded 15 ug m-3. Stemming from the strong aging process under high relative humidity condition, freshly emitted BC particle was observed to turn into internally mixing within a short time scale. To understand the variation of the hygroscopicity of BC during its aging process, the hygroscopic growth factor of BC-containing particles was measured with a combination of a hygroscopic tandem differential mobility analyzer and a SP2. The particle hygroscopic growth factor of the volume fraction of BC. And a minor number fraction of the more-hygroscopic mode particles was observed to contain BC cores.

7-2 High time-resolved optical and chemical characterisation of wintertime aerosol in Rome (Italy): case studies

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Atmospheric aerosol is a complex mixture of particles with a huge variability in terms of physicalchemical properties. Even though current European air quality regulations refer to 24-hour limit values, atmospheric processes and emission sources contributions affect aerosol concentration, chemical composition, optical properties, size distribution and toxicity on shorter time scale.

During February 2017, the Carbonaceous Aerosol in Rome and Environs (CARE[1]) experiment was carried out in Rome using various instruments and techniques in order to obtain a comprehensive picture of the aerosol properties in a Mediterranean urban background site during wintertime, when combustion sources typically show the largest contribution to PM levels.

In this work, we present a study on the phenomenology of high time-resolution (from 1 minute to 2 hours) physical-chemical properties of the aerosol investigated in the framework of the CARE experiment. In particular, wavelength dependent scattering and absorption coefficients, chemical speciation, and particle number size distribution are used to analyse in detail some peculiar events and atmospheric conditions that took place during the CARE campaign, with the aim of finding out a possible combination of parameters that can be used as a metric to clearly identify aerosols with different origin.

The inter-comparison of different instruments and measurement techniques proved to be of great help at identifying specific episodes. In fact, some aerosol properties can differ significantly from the average ones during peculiar events, while some others are not sensitive to an even strong change in atmospheric conditions. Indeed, for the CARE campaign the combination of scattering and absorption wavelength dependences allowed to clearly identify a sea salt advection and a Saharan dust transport episode that could not have been distinguished focusing on one optical parameter only. These events were also confirmed by both the detailed elemental speciation performed on samples collected at 1h time resolution, which highlighted the increment in concentrations of typical marine/crustal elements during the two events, and particle number size distributions showing a corresponding high number of coarse particles. Finally, the Scattering and Absorption Ångström Exponents (SAE and AAE, respectively) calculated with different λ pairs showed that attention has to be paid when applying optical apportionment models, since the choice of the suitable wavelengths is essential in order to avoid data misinterpretation.

[1] Costabile et al. (2017). Atmosphere 8, 249.

7-3 Continuous observations of aerosol optical and chemical properties in Western Europe at the Juelich Meteo Tower - Results from the first full year

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The way airborne aerosols impact climate, either by scattering light or by absorbing it, is well known and documented. The overall effect on the radiation budget depends on three main aerosol characteristics: optical depth, single scattering albedo and backscatter fraction (Haywood and Shine, 1995). Although the aerosol and light interaction mechanism is deeply understood, the quantification of the aforementioned impact still presents major uncertainties.

In 2015 a new technology was presented for measuring single-scattering albedo using a single instrument, the Cavity Attenuated Phase Shift Single Scattering Albedo Monitor (CAPS PM_{ssa}), developed by Aerodyne, Inc. An instrument, operated here at 630 nm wavelength, was previously assessed in a multi-instrument optical closure study in the laboratory using controlled particle generation systems and known particle compositions (Faria *et al.*, 2016). The results obtained showed excellent agreement with proven technology for both absorption and scattering measurements.

Following the laboratory study, in August 2016 a suite of instruments was deployed at the bottom of a meteorological tower located in Jülich, Germany. Ambient air was sampled from three different heights, 10, 50, and 120 m. The instruments used are described below:

- 2x CAPS PM_{SSA} (Aerodyne Inc.): (630, 450 nm); particle single scattering albedo
- Aurora 4000 Nephelometer (EcoTech): (635, 525 and 450nm); scattering
- TSI 3563 Nephelometer (TSI): (700, 550 and 450nm); scattering
- PSAP (Radiance Research): (660, 530 and 467nm); absorption
- TAP (Brechtel): (652, 528 and 467nm); absorption
- CPC (GRIMM): particle number concentration
- OPC (GRIMM): (655nm) particle number concentration and size distribution
- HR-AMS (modified, Aerodyne Inc.): mass concentration and chemical analysis

The multi-instrumental optical closure study during the long term campaign showed good agreement. A few differences were spotted and have been more intensively studied; for instance, the absorption Ångstrom exponents from the TAP and PSAP instruments did not always agree.

The results obtained over the 2 years monitoring campaign have shown many interesting aspects such as the atmospheric aerosol stratification under specific meteorological conditions. It was also possible to observe seasonal trends on aerosol characteristics like size distributions, and mass loading.

Chemical information was also obtained by using the data acquired by the HR-AMS and by the study of the calculated absorption Ångstrom exponent. A few interesting periods were also selected for further study, e.g., the forest fires in the Iberian Peninsula in October 2017. This event was also observed by the remote sensing station located in Jülich (JOYCE - Jülich Observatory for Cloud Evolution, Löhnert *et al.* (2015)). The instrument inter-comparison will also be discussed. First attempts to source apportion the

7-4 Multi-wavelength aerosol absorption coefficient measurements: instrument inter-comparison and results of source and source-component modelling

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In this work, some results obtained in the frame of a comprehensive measuring campaign carried out within the COST COLOSSAL activities at an urban background station at the University of Milano-Bicocca (Italy) will be presented. The work aims to gain insight into the performances of:

· different instruments for the determination of the aerosol absorption coefficient (babs);

· different models based on multi-wavelength (multi- λ) babs data to identify light absorbing aerosol sources (fossil fuel, FF; biomass burning, BB) and/or components (Black Carbon, BC; Brown Carbon, BrC).

Twelve-hour resolved aerosol samples were collected on pre-fired (700°C, 1h) quartz fibre filters by a low volume sampler (flowrate 1m3/h). The samples were analysed by the multi- λ polar photometer PP_UniMI[1,2] at the University of Milan for off-line babs determination, by Thermal-Optical Transmittance analysis (EUSAAR_2 protocol) for OC/EC and by HPAEC_PAD for levoglucosan at the University of Genoa. The site was also equipped with on-line instrumentation -Aethalometers AE31 and AE33 (Magee Scientific), and a Multi-Angle Absorption Photometer MAAP (Thermo-Fischer) - providing information on BC from babs determination.

The babs from PP UniMI and MAAP (data averaged to filter sampling time resolution) agreed very well. A high correlation (R=0.96) was found also between MAAP/PP UniMI and Aethalometer data, but results from both AE31 and AE33 featured slopes significantly higher than 1 relative to the MAAP/PP UniMI when using the Aethalometer tape specific multiple scattering parameter CAE31= 2.14 and CAE33= 1.57. Higher values of these parameters (e.g. CAE33>2.5) seem necessary to obtain the realistic babs from Aethalometers. Opposite, BC data from on-line instruments showed lower discrepancy, probably due to the different mass absorption crosssections (also considering the different λs of operation) set in the instruments. Multi- λ Aethalometer babs measurements were used as input to the Aethalometer model[3] and the Multi-Wavelength Absorption Analyzer (MWAA) model[4] for source and source-component apportionment, respectively. As for the Aethalometer model, a multi- λ fit was also attempted instead of choosing two fixed λs as performed in the literature. Differences depending on the chosen λ s range were noticed with both approaches. The MWAA model provided α BrC estimate (3.8±0.4 considering the 470-950 nm range) during the campaign, in addition to BC and BrC apportionment. An episode characterised by unusual BrC contribution (identified by high Ångstrom absorption exponent in Aethalometer data) was identified and deeply investigated in terms of model performance.

[1] Vecchi et al., J. Aerosol Sci., 2014, 70, 15–25.

- [2] Bernardoni et al., J. Aerosol Sci., 2017, 107, 84-93.
- [3] Sandradewi et al., Environ. Sci. Technol., 2008, 42, 3316-3323.
- [4] Massabò et al., Atmos. Environ., 2015, 108, 1-12

7-5 Optical Characterization of Fresh and Photochemically-Aged Aerosols Emitted from Laboratory Siberian Peat Burning

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Carbonaceous aerosols emitted by biomass burning greatly influence radiative forcing and climate on regional and global scales. In this study, we characterized the optical properties of emissions from the laboratory combustion of Siberian peat. This fuel frequently burns in large and longlasting wildland fires affecting boreal and arctic ecosystems. Peat burns mostly in smoldering combustion, emitting large amounts of organic and brown carbon. Here, we characterized the optical properties of both fresh and photochemically-aged emissions. Atmospheric aging was simulated using an Oxidation Flow Reactor (OFR), which was operated with different ultraviolet actinic fluxes to simulate atmospheric aging on timescales ranging from days to months. Aerosol characterization utilized real time instruments including a photoacoustic three-wavelength soot spectrometer (PASS) and a scanning mobility particle sizer (SMPS) with additional analysis of aerosols collected on quartz and Teflon filters. Three-wavelength optical properties of fresh and aged aerosols including single scattering albedo and absorption and scattering Ångström exponents will be presented. In addition, retrieval of complex refractive indices will be discussed.

7-6 Experimental determination of black and brown carbon heating rate from mid-latitudes to the Arctic ocean, and related energy gradient

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Black carbon (BC) and Brown Carbon (BrC) absorbs sunlight and heat the atmosphere[1]. The heating rate (HR) determination is, up to now, too sparse, does not account for light-absorbingaerosol (LAA) speciation and for the influence of different cloudy sky conditions[2,3]. This work applies a new method[4] to experimentally determine the HR induced by the LAA in the context of LAA species (BC, BrC), and sources (fossil fuel, FF; biomass burning, BB)[5]. The methodology is based on the direct determination of the radiative power density absorbed into a ground-based atmospheric layer determined coupling spectral aerosol absorption measurements (Aethalometers (AE31 and AE-33, Magee Scientific, $7-\lambda$) with the spectrally resolved measurements of the direct, diffuse and reflected radiation (Multiplexer-Radiometer-Irradiometer ROX and SPN1 radiometer) [4].

This method was applied first in Milan from 2015 to 2016 and time-resolved measurements (5 min) of *HR* were performed determining: 1) the seasonal behavior of *HR* (winter: 1.83 ± 0.02 K day-1; summer: 1.04 ± 0.01 K day-1); 2) the daily cycle of *HR*; 3) the *HR* in different sky conditions (from 1.75 ± 0.03 K day-1 in clear sky to 0.43 ± 0.01 K day-1 in complete overcast); 4) the apportionment to different sources: *HR*FF (0.74 ± 0.01 K day-1) and *HR*BB (0.46 ± 0.01 K day-1); 4) the *HR* of BrC (*HR*BrC: 0.15 ± 0.01 K day-1, $12.5\pm0.6\%$ of the total) and that of BC (*HR*BC: 1.05 ± 0.02 K day-1; 87.5 $\pm0.6\%$ of the total).

Moreover, the Oceania research Vessel of the Institute of Oceanology, Polish Academy of Sciences, was equipped with the same instrumentation and the HR was experimentally determined from midlatidudes to the Arctic along the AREX2018 oceanographic cruise. The *HR* showed a clear latitudinal behavior with higher values in the harbor of Gdansk (0.46 ± 0.01 K/day) followed by the Baltic Sea (0.06 ± 0.01 K/day), the Norvegian Sea (0.02 ± 0.01 K/day) and finally with the lowest values in the pure Arctic Ocean (0.005 ± 0.001 K/day).

They followed the decrease of both BC concentrations and global radiation from 1189 ± 21 ng/m3 and 230 ± 6 W/m2 (Gdansk) to 27 ± 1 ng/m3 and 111 ± 3 W/m2 (Arctic Ocean). The latitunal gradient of the HR clearly demonstrate the hypothesis[6] that the warming of the Arctic could be due to a heating transport. In this respect, the LAA added about 500 J/m3 at mid-latitudes and only 5 J/m3 close to the North Pole. During the lecture also the role of LAA species and sources will be discussed.

Acknoledgements: Project MIUR – Dipartimenti di Eccellenza 2018–2022.

References:

Bond et al., J. Geophis Res., VOL. 118, 1–173, doi:10.1002/jgrd.50171, 2013.

Samset et al., Atmos. Chem. Phys., 14, 12465–12477, 2014.

Ferrero et al., Atmos. Chem. Phys., 14, 9641–9664, 2014

Ferrero, L., et al (2018) Environ. Sci Tech., under review.

Massabò, D., et al (2015) Atmos. Environ., 108, 1-11.

Shindell and Faluvegi (2009). Nature Geoscience, vol 2, april 2009.

7-7 Investigation of enhancement in the mass absorption crosssection of black carbon aerosols (MACBC) at a rural site in central Europe (Melpitz, Germany)

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In order to estimate the direct radiative forcing of black carbon (BC), climate models infer the total light absorption from simulated BC mass by means of the mass absorption cross section of BC (MACBC). MACBC depends on BC refractive index, size, shape and mixing state with other aerosol components. Amongst these factors mixing state is especially important due to the so-called 'lensing effect', i.e. the increase of the MACBC of a BC particle by non-absorbing coatings. Conceptually, we define the MAC enhancement factor due to coatings, EMAC, as the ratio of the MACBC of a BC particle divided by the MACBC of its BC core in bare form. According to theoretical simulations and laboratory experiments, EMAC varies between 1 and 3 (Samset et al., 2018) depending on the degree of internal mixing (e.g. BC volume fraction) and the morphology and position of the embedded BC core (Adachi et al., 2010). However, due to the limited ambient measurements of EMAC, it is not clear to what degree variations of MACBC are caused by variations in degree of internal mixing of BC alone.

Properties of atmospheric BC particles were characterized during a field experiment in Melpitz, Germany in February 2017. Aerosol light absorption at 870 nm was measured with a Photoacoustic Extinctiometer and BC properties (BC mass concentration, core size distribution and coating thickness) were measured with a Single Particle Soot Photometer. Additionally, a catalytic stripper was used to cyclically remove BC coatings. From these data we inferred EMAC by dividing the MACBC values measured for ambient (untreated) BC particles by that of denuded BC particles. Observed EMAC values ranged from 1.05 to 1.4 for ambient BC with low to moderate coating thickness. MACBC and EMAC were strongly correlated with coating thickness, while no clear relationship between MACBC and mean BC core size was found. These results show that the lensing effect occurs and that it is a main driver of the variations in MACBC, while changes in BC core size play only a minor role.

References

Samset et al., 2018, Curr. Clim. Change. Rep., 4: 65.

Adachi et al., 2010, J. Geophys. Res., 115, D15206.

Chapter 2

Posters

- 2.1 Secondary organic aerosol formation
- 2.2 Analytical techniques and methods
- 2.3 Source characterization and source apportionment
- 2.4 Aerosol concentrations, trends and transport measurements and models
- 2.5 Carbonaceous CCN and INPs
- 2.6 Bioaerosols
- 2.7 Optical properties of carbonaceous aerosols, radiative forcing and climate

Poster Session 1

2.1 Secondary organic aerosol formation
P1-1 New Aspect of Aqueous-Phase Nitration of Methylcatechol by Means of Electrochemistry

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Organic pollutants, which are primarily emitted into the atmosphere, continue to react in the gas and atmospheric aqueous phase, and also on the surface of carbonaceous particles. There are more and more evidences that chemical processes in the atmospheric aqueous phase (i.e., cloud, fog and aerosol water) can efficiently contribute to organic compounds aging, and thus to secondary organic aerosol (SOA) formation [1,2]. Atmospheric aqueous-phase chemistry can also contribute to the formation of chromophores and absorbing SOA, known as atmospheric brown carbon (BrC), the term referring to the light-absorbing organic matter, which absorbs light in the near-ultraviolet and blue range, and so influences the climate by radiative forcing.

Little is still known about the mechanisms of BrC formation. Important precursors for BrC are aromatic compounds, which contribute significantly to the budget of atmospheric pollution. Of great importance are substituted aromatics, such as catechol, 3-methylcatechol (3MC), hydroquinone and resorcinol [3]. Methylnitrocatechols (MNCs) are recognized as BrC constituents [4] and their formation mechanism has been recently extensively studied [5]. The dominant pathway of 3MC transformation to its nitrated products (3-methyl-5-nitrocatechol and 3-methyl-4-nitrocatechol) in the presence of nitrous acid/nitrite (HNO2/NO2–) involves two consecutive reactions; oxidation and nitration by addition. It is assumed that, during the oxidation by HNO2, 3-methyl-*ortho*-quinone (3M*o*Q) is formed, which in the presence of NO2– undergoes the conjugated addition forming different nitro products.

Using nitration of 3MC as a case example, we demonstrate a novel experimental platform for studying homogeneous reaction mechanisms in a condensed phase. To confirm the proposed mechanism and the presence of assumed intermediate (3MoQ), each individual step of the complex reaction mechanism (oxidation and nitration) had to be isolated and separately studied. For this purpose, electrochemistry was used for the generation of reactive intermediate.

Reference

[1].Y.B. Lim, Y. Tan, M. J. Perri, S.P. Seitzinger, and B.J. Turpin (2010), Atmos. Chem. Phys. 10, 10521-10539

[2] B. Ervens, B.J. Turpin, R.J. Weber (2011), Atmos. Chem. Phys. 11, 11069-11069.

[3] E.H. Hoffmann, A. Tilgner, R. Wolke, O. Boge, A. Walter, and H. Herrmann (2018), Phys. Chem. Chem. Phys. 20, 10960-10977.

[4] S. Frka, M. Šala, A. Kroflič, M. Huš, A. Čusak, and I. Grgić (2016), Environ. Sci. Technol. 50, 5526-5535.

[5] K. Vidović, D. Lašič-Jurković, M. Šala, A. Kroflič, I. Grgić (2018), Environ. Sci. Technol. 52, 9722-9730.

P1-2 Quantification of Primary and Secondary Organic Aerosol Particles collected in remote North Western Vietnam during pre-monsoon season

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Biomass Burning (BB) is amongst important sources emitting to atmospheric trace gases and particles on both global and regional scale. After primary emission, smoke plumes go through complex physical and photo-chemical processes during transport which results in the formation of secondary organic aerosol. Northern Southeast Asia is well-known for intense and recurring biomass burning emission from forest wild fires, and after-harvest crop burning during pre-monsoon season from February to April, which influences the large-scale atmospheric circulation in Northern Southeast Asia, where organic chemistry study is still limited.

Measurement campaigns were performed at Pha-Din remote mountainous station during biomass burning season from late March to early April in 2015. PM2.5 was collected on quartz fiber filters by MiniVol sampler with 24h sampling protocol for subsequent analysis from 23 March to 12 April 2015. Here we report the temporal variations of primary organic aerosol, such as anhydrous sugars, resin and lignin compounds, and secondary organic aerosol, i.e. nitrophenols, in order to characterize the primary and secondary aerosol loading in remote background region and its aging implication.

Levoglucosan, produced during pyrolysis of cellulose, is a general tracer for biomass burning (BB) aerosols, averaged at 379 ± 506 (23-1712) ng m–3, indicating a significant impact of BB to the aerosols. Further wood combustion products originating from resin and lignin breakdown, including acetosyringone, vanillic acid, vanillin, m-hydroxybenzoic acid, p-hydroxybenzoic acid, and syringealdehyde were found during sampling campaign. Total resolved resin and lignins averaged at 79 ± 109 (2-369) ng m–3, in which the predominance are m,-p- hydroxybenzoic acid and syringic acid, which implies the emissions from vegetation and hardwood combustion. Nitrophenols, i.e. organic molecules that contain at least one nitro group (NO2-), are oxidation products of phenols, nitrobenzene... in several chamber studies on secondary organic aerosol. We found in our samples 4-Nitrophenol, 4-Nitrocatechol, and 2,6-Dimethoxy-4-nitrophenol, and they averaged at 8 ± 14 (1-60) ng m–3, 70 ± 140 (1-616) ng m–3, 0.9 ± 1.5 (0.1-6.1) ng m–3, respectively. Interestingly, 4-Nitrophenol and 4-Nitrocatechol peaked on the day April 05 & 06, 2015, which indicated the great extent of aging of transported aerosol at receptor site during sampling campaign.

The temporal variation of primary and secondary aerosol compounds showed the distinctive pattern of non-intensive BB (local) vs intensive BB period (long-range transport). The comparison of organic molecular tracers together with HYSPLIT model indicated the influence of biomass burning smokes from the transport pathway of the Southeast Asian continental outflow when westerly winds prevailed.

This work was financially supported by DAAD (Deutscher Akademischer Austauschdienst) via research grant No.91614707.

P1-3 Persistent indoor secondary organic aerosol formation due to a single usage of a kitchen detergent

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As people spend approximately 80% of their lives indoors, the indoor aerosol levels are at least of the same importance as outdoor ones due to their negative health effects. Despite their importance, little is known about transformations of indoor aerosols under the effect of chemicals used in our homes. One of chemicals being present in kitchen detergents is mono-ethanol amine (MEA). Using such detergent and consequences related to indoor carbonaceous aerosol are described in this study.

The offline PM1 and PM10 samples, and cascade impactors were used to collect aerosol samples in both indoors and outdoors in parallel. All samples were analysed using ion chromatography. More details can be found in Talbot et al. (2016). Online chemical composition was obtained using aerosol mass spectrometer (AMS) used in cycle consisting from 10 min indoor and 10 min outdoor sampling using automated switching valve. OC and EC were monitored both indoors and outdoors by two field Sunset OC/EC analysers.

In this study, the influence of a W5 degreaser (Lidl, Germany) containing more than 5% (w/w) of MEA, sprayed on kitchen furniture surfaces, is analysed.

The results showed sudden change in NR-PM1 composition after the detergent usage. First, particles from spray itself made a peak in organic aerosol concentrations followed by its exponential decay. However, in the same time, transformation of $(NH_4)_2SO_4$ and NH_4NO_3 started, forming secondary MEA sulphates and MEA nitrates and increasing the total amount of OC in the indoor aerosol. The process continued until the doors and windows were opened. The period between spraying and opening the windows took more than 15 h during the first and 48 h during the second experiment. Some influence of MEA was also seen on two next days despite ventilation of the room and cleaning the surfaces during the first experiment. Paper towels used for cleaning surfaces were left in a basket and served probably as source of MEA for further reaction. Evaporation from other surfaces was also possible source of MEA.

Beside this effect, the transformation of ammonium nitrate to MEA nitrate increased stability of nitrate aerosol in indoor environment and therefore exposure by nitrates increases substantially as the result of ammonium to amminium nitrate transformation. More can be found in Schwarz et al. (2017).

This work was supported by EU FP7 under grant agreement No. 315760 HEXACOMM , and by MEYS CR in frame of projects ACTRIS-CZ – LM2015037 and INTER-COST LTC18068.

REFERENCES

Talbot, N., Kubelová L., Makeš O., Cusack M., Ondráček J., Vodička P., Schwarz J., Ždímal V., (2016) Atmos. Environ. 131, 171–184.

Schwarz J., Makeš O., Ondráček J., Cusack M., Talbot N., Vodička P., Kubelová L., Ždímal V. (2017), Environ. Sci. Technol. 51(11), 5907-5912 (2017).

P1-4 New Particle Formation and Sub-10nm Size Distribution Measurements in Paphos, Cyprus, during the A-LIFE field experiment

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Atmospheric new particle formation (NPF) is a frequent phenomenon that is significantly contributing to the global aerosol budget throughout the troposphere. Newly formed particles can affect human health and potentially grow to sizes large enough to influence the Earth's radiation balance and climate.

In this study, we aim at characterizing NPF and early nanoparticle growth in the Eastern Mediterranean region during the ERC-funded A-LIFE (Absorbing aerosol layers in a changing climate: aging, LIFEtime and dynamics) field experiment. The A-LIFE intensive measurement campaign in April 2017 combined in-situ and remote sensing measurement techniques both at the ground and on the Deutsches Zentrum für Luft- und Raumfahrt (DLR) research aircraft Falcon.

The understanding of the processes leading to NPF requires particle measurements down to the critical size of freshly formed particles. Sub-10nm particle size distribution measurements are extremely challenging due to high diffusional loss rates in the sampling and measurement system. Novel measurement techniques enable the detection of newly formed particles at a decent sensitivity: the DMA-train, designed for sub-10nm size distribution and precise growth rate measurements, was first set up in an atmospheric experiment. Furthermore, a SMPS covered the size range 10 - 800 nm at 5 min time resolution and a total CPC measured the total particle concentration.

During the 27-day measurement period at the coastal ground-based station in Paphos, we observed 7 NPF events during morning hours and were able to follow the initial particle growth in the DMA-train in 3 cases. In 2 cases, however, the initial growth stopped below 10 nm. This finding suggests that NPF may happen much more frequently than is currently thought but is oftentimes not captured well enough by regular SMPS. Following the formation and early growth of particles, we observed that particles further grow into a size range that is relevant to cloud droplet activation.

The local wind pattern is dominated by a land-sea-breeze system with NE and NW being the prevailing wind directions. The typical diurnal picture reveals highest total particle concentrations together with elevated NO/NO_2 and SO_2 concentrations for air masses carried to the station from the interior of the island during night time. NPF events were found during both easterly and westerly winds. Furthermore, we use the FLEXPART (FLEXible PARTicle dispersion model) model in order to better understand on a large scale the origin of air masses that favour NPF.

In our presentation, we present results from the A-LIFE field experiment with the special focus on the parameters influencing NPF and initial particle growth in Cyprus. We will include size distribution data obtained by the DMA-train and correlations between particle and trace gas data as well as meteorological parameters. In addition, the backward trajectory analysis from FLEXPART and possible implications on NPF will be discussed.

2.2 Analytical techniques and methods

P1-5 Laser desorption of aromatic compounds from carbonaceous aerosol surrogates and determination of their adsorption energy

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Extensive global emission of fine and ultra-fine carbon-based particulates presents a well-known health risk and raises significant environmental concern. The toxicity of carbonaceous particles, soot in particular, is mainly determined by their surface composition and reactivity. It is thus important to have information on the actual interaction (physisorption, chemisorption) of adsorbates with the particle surface, and to have an estimate of the adsorption energy. This, however, can be an arduous task for a "real-world" soot particle bearing a multitude of molecular species. Among the variety of molecules which can be encountered on a soot particle surface, Polycyclic Aromatic Hydrocarbons (PAH) are of great importance, both for fundamental mechanisms (crucial role in soot nucleation and growth) and for toxicology issues (proven carcinogenic effect).

In this study, we propose an original method for measuring the adsorption energy of PAHs to a carbon substrate. This method is using a pulse-to-pulse signal of a two-step laser mass spectrometer, developed in our lab over the last decade to probe the chemical composition of soot particles with high sensitivity and selectivity (Faccinetto *et al, Environ Sci Technol,* 2015). To validate the method, we prepared "surrogate soot" samples by adsorbing well-determined amounts of several PAHs onto black carbon particles, thus allowing us to work in controlled conditions in terms of adsorbates surface concentration.

Two approaches are derived and used for the measurement of the adsorption energy. For the first one, the signal for the PAH of interest is measured for a multitude of successive desorption laser pulses. The data is then fitted with a pseudo-exponential decay (number of desorbed molecules vs number of applied laser pulses). The second method consists in recording the "fluence curve" - the variation of the signal intensity with the desorption laser fluence. The signal corresponding to the first laser shot was recorded for a multitude of laser fluences and enabled us to, once again, retrieve the adsorption energy of different PAHs onto the black carbon surface. These two different approaches complement each other, thus helping to obtain a more precise result by reducing the uncertainties induced by possible non-homogeneous surface concentration and/or fluctuations in laser fluence.

The new method was initially based on the assumption of quasi-thermal desorption of molecules (steady-state approximation) at low laser fluences (Dreisewerd *et al*, *Int J Mass Spectrom*, 1995). A more detailed model, taking into account the fast temperature change associated with laser desorption, was also developed. A comparison of the two models will be presented.

First results obtained for pyrene and coronene adsorbed on black carbon show good agreement with values reported in the literature, thus serving as a proof of concept for the new method. Application of this method to "real soot" characterization will be discussed.

P1-6 Comparison of ICP-MS and LA-ICP-MS Methods for the Determination of Elemental Composition of PM10

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Awareness about air pollution and its connection to diseases is increasing. Traffic, industry, combustion processes and other emission sources are daily releasing a lot of particulates in the air. Dangerous fraction of problematic aerosols are inorganic components, mostly metals. Therefore, precise and accurate analytical methods for their determination are needed, to allow for appropriate assessment of the related health effects and accurate source apportionment for planning exact preventive measures.

The standard SIST EN14902:2005 published by the European Committee specifies the method for the determination of particulate lead (Pb), cadmium (Cd), arsenic (As) and nickel (Ni) in ambient air. This standard determines pre-treatment of PM10 air filters by microwave digestion and analysis by graphite furnace atomic absorption spectrometry (GFAAS) or inductively coupled plasma mass spectrometry (ICP-MS). The pre-treatment requires concentrated acids and is therefore environmentally unfriendly and time consuming. Sampling by laser ablation for the ICP-MS analysis, on the other hand, does not require any pre-treatment. Therefore, we recognize laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) much more sustainable and faster technique for the analysis of ambient PM on filter samples.

In our work we first measure the concentrations of 10 elements (Pb, Cd, As, Ni, Ba, Cr, Cu, Zn, Al, Se) in PM10 on quartz-fiber filters by microwave digestion and ICP-MS (according to the EN14902:2005), and secondly optimize the parameters of laser ablation for their determination by LA-ICP-MS.

Analytical procedure according to EN14902:2005 was first optimized for the time of microwave digestion and temperature program, subsample size, dilution factor and vessels cleaning procedures. In the digestion step only HNO₃ and H_2O_2 reagents are prescribed and therefore quartz filter is not completely (if at all) digested. This also raises doubts about the digestion of PM material deposited on the filter, or at least its inorganic fraction, as we cannot be sure that it is fully digested during the prescribed digestion protocol.

With laser ablation the bias of pre-treatment is avoided. Laser ablation is applied directly to the solid PM on air filter and parameters like laser spot size, scan speed, repetition rate, fluency and the sampling area were optimized. Homogeneity of the filter was studied with sampling across the radius of the filter.

We find out that elemental analysis of PM10 quartz-fiber filters by LA-ICP-MS is a viable alternative to microwave assisted digestion and ICP-MS, due to bypassing the pre-treatment step and the possibility of accurately measuring more elements than specified in the current standard.

Reference:

EN 14902:2005, Ambient Air Quality-Standard Method for the Measurement of Pb, Cd, As and Ni in the PM10 Fraction of suspended Particulate Matter, CEN, Brussels, 2005.

P1-7 Methods for the separation of gaseous and particulate-bound species in combustion emissions

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PAHs are considered as the "building blocks" of soot particles during combustion processes. They are widely known to have a negative impact on human health considering their carcinogenic and mutagenic properties. Many studies have focused on the characterization of the soot surface. However, the lightest part of the aromatic compounds can remain in the gas phase and the two phases can affect human health. It is therefore important to work simultaneously on gas phase and particle-related PAHs to better understand their role in combustion processes, as well as their impact on the environment and human health. In this study, we present original methods for separating gaseous PAHs and particles using either two successive filters or an impaction on specific substrates. The methods were tested on different soot generators, including the CAST and laboratory flames. In the first method, a "frontal" filter is used to capture (mainly) the particles emitted by combustion, while most of the gaseous phase passing through this filter is captured by the "back" filter covered with a layer of carbon. Black. In the second method, spatial segregation is used to differentiate the phase origin of the species. Two-stage laser mass spectrometry (L2MS) and / or secondary ion mass spectrometry (SIMS) were applied to various samples to differentiate the chemical composition of the particulate and gas phase fractions. With good selectivity for aromatic compounds, L2MS can provide non-fragmented chemical information, while SIMS with higher resolution is sensitive to inorganic and organic species. The soot particles on the front filters contain high mass PAHs (semi-volatile and non-volatile PAHs), while only lower mass PAHs (volatile and semi-volatile species) up to 250 m / z have been detected. on the back filters. Multivariate analysis was applied to better distinguish the two phases of the source operating conditions. Finally, a possible application to the separation of gas / particle phases from an original method based on the adsorption energy of PAHs, recently developed in the PhLAM laboratory, will be discussed.

P1-8 Evaluation of the Aerosol Dynamics Inc. concentrator for Aerosol Chemical Speciation Monitor

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Measurement of the chemical characteristics of particles often benefit from higher sample load that can be achieved e.g. by increasing sample flow rate, longer sampling times or by using particle concentrator. Enrichment of particle number or mass concentrations is particularly important for the measurements in the regions where particle concentrations are low and a long integration time is needed, or for studying individual aerosol trace components such as metals.

Here we present field tests conducted with a new air-to-air particle concentrator, the Aerosol Dynamics Inc. concentrator (ADIc). ADIc system is designed specifically for instruments with low sampling flow rates on the order of 0.1 L/min like used in aerosol mass spectrometer instruments. ADIc was tested at the field at an urban background station (SMEAR III) in Helsinki, Finland from July 13 to October 22, 2018. Ambient particles were sampled through a 2.5 mm cyclone with a flow rate of 3 L/min. Sample flow was split into two sampling lines; first line went to the ADIc followed by a quadrupole Aerosol Chemical Speciation Monitor (Q-ACSM, Ng et al., 2011) and the second line to the Soot Particle Aerosol Mass Spectrometer (SP-AMS, Onasch et al., 2012).

The ACSM data was collected with approximately 10-minute time resolution and the SP-AMS data, measured with a time resolution of 1.5 minutes, and was averaged to the ACSM time periods. Two sample flow regimes were tested with the ACSM+ADIc system; the sample flow was set to either 1.7 L/min or 1.0 L/min while the output flow of the ADIc was determined by the ACSM inlet flow of 0.08 L/min, giving a theoretical concentration factor (CF) of 21 and 12.5 for high and low sample flow, respectively.

The time series of all chemical species (organics, sulfate, nitrate, ammonium, chloride) measured with the ACSM+ADIc and SP-AMS track each other well and the average mass loadings agreed within 20–30%. In terms of Q-ACSM measurement, a particularly important improvement in signal to noise with the ADIc was achieved. Use of the ADIc with the ACSM provides better estimates of collection efficiency (CE) for ambient aerosol as higher concentrations of inorganics especially ammonium are beneficial for calculation of inorganic ion balance. In addition, better signal to noise for tracer m/z's will improve source apportionment with statistical methods such as positive matrix factorization

References:

Ng, N.L. et al., Aerosol Sci. Technol., 45: 770–784, 2011.

Onasch, T. B. et al., Aerosol Sci. Technol., 46: 804–817, 2012.

P1-9 The measurements of the content of coal particles in dust suspended in Poland

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Air quality is an extremely important component of the environment due to the fact that it determines the quality of human life. Air pollutants have their sources in both natural and anthropogenic processes. However, in an industrialized area, anthropogenic sources, both local and transported over long distances, are predominant. The urban aerosol contained in the atmospheric air is a complicated substance whose physical and chemical properties depend on concentration, chemical composition and particle size. In Poland, the main source of energy supply is hard coal. As a result of the process of burning coal, many harmful substances are emitted into the atmosphere, among others dust. Extremely harmful to human health and the environment of the dust component are carbon particles that may contain polycyclic aromatic hydrocarbons or heavy metals. The main sectors related to the combustion of solid fuels in Poland are: the energy production and transformation sector (power plants and combined heat and power plants), the communal and housing sector, communications, industry, production processes, mineral and natural raw materials processing, agriculture. Aerosol coal particles, in contrast to its other components, have the ability to absorb solar radiation, thus contributing to the warming of the climate. In addition, the carbon particles are a very fine fraction, penetrating along with the inhaled air into the interstitial lung tissue together with harmful substances attached to the surface of these particles. For these reasons, many years of research into the content of carbonaceous matter in dust pollution is carried out in Poland. Total carbon (TC) consists of elemental carbon (EC, elemental carbon), organic carbon (OC, organic carbon) and inorganic carbon (IC, inorganic carbon). elemental carbon emitted to the atmosphere is considered as primary pollution (POC, primary organic carbon), while organic carbon can be a primary or secondary pollution (SOC, secondary organic carbon). This work discusses the methodology of measuring the carbon particles and presents the most important results of the research. The measurements are carried out at two stations: a site recognized in accordance with Directive 2008/50 / EC for the background location - in Racibórz and a site recognized in accordance with the same directive for the urban station - in Zabrze. The work analyzes the OC / EC variation in PM2.5 as a function of classification of circulation types. The share of primary and secondary coal in total PM2.5 was also calculated. The obtained results indicate seasonal variation in carbon particle concentrations and their share in the total PM2.5 dust fraction. Interpretation of the results allows to determine the impact of local emission and longdistance transport on the physicochemical composition of selected aerosol fractions.

P1-10 Two-wavelength thermo-optical determination of Black and Brown Carbon in atmospheric aerosols

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Carbonaceous aerosol (CA) plays an important role in many different issues ranging from human health to global climate change. It mainly consists of organic carbon (OC) and elemental carbon (EC) although a minor fraction of carbonate carbon could be also present.

Thermo-optical analysis are widely adopted for the quantitative determination of total, TC, organic, OC and elemental, EC, Carbon in aerosol samples collected on quartz fibre filters. Nevertheless, the methodology presents several issues in particular about the artefacts related to the formation of pyrolytic carbon. It is usually neglected the uncertainty due to the possible presence of brown carbon (BrC) in the sample under analysis, i.e. the optically active fraction of OC produced by biomass burning and with characteristics intermediate between OC and EC.

The Sunset EC/OC analyser unit at the Physics Department of the University of Genoa has been modified, making possible the alternative use of the standard laser diode at $\lambda = 635$ nm or of a laser diode at $\lambda = 405$ nm, to monitor the optical transmittance during the thermo-optical analysis. The additional use of the 405 nm transmittance measurement provides valuable information about the composition of the sample (i.e. the presence of Brown Carbon (BrC), that is part of OC but also a light absorbing species and can shift the split point (Andreae & Gelencsér, 2006)) as well as on the pyrolytic carbon formation, both able to affect the instrumental "split point" (i.e. the moment of the analysis in which the laser transmittance is back to its starting value, thus defining EC/OC separation).

We present here the new instrument set-up, tested using both synthetic and real (urban and rural) aerosols, collected on quartz fibre filters.

The first test was the analysis of synthetic samples prepared with a solution of Aquadag (i.e. a water-based colloidal graphite suspension) which can be considered as composed by EC/BC only. Samples were analysed with both NIOSH5040 and EUSAAR_2 protocols. Then other samples prepared with a solution of ammonium sulphate (NH4)2SO4 in Aquadag were analysed as well to mimic the behaviour of real-world aerosol samples (i.e. with a scattering compound mixed to the absorbing Aquadag spherules). This second set of samples was analysed through the EUSAAR_2 protocol only. Finally, a set of real PM10 samples from an urban area of the city of Genoa (IT) whit negligible contribute of biomass burning to PM composition (Bove et al., 2014) was used.

After this characterization phase, the modified Sunset set-up was used for the first time, in conjunction with the MWAA instrument and apportionment methodology (Massabò et al., 2015), to retrieve the MAC (Mass Absorption Coefficient) of Brown Carbon at the two wavelengths of $\lambda = 635$ nm and $\lambda = 405$ nm, in a set of samples collected wintertime in a mountain site. Results turned out to be well correlated with Levoglucosan concentrations determined on the same aerosol samples.

P1-11 A technique for direct measurements of dry and wet deposition of black carbon aerosol

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The atmospheric lifetime of black carbon (BC) is controlled by wet and dry deposition, which are poorly constrained by observations. We show that the single particle soot photometer (SP2) can measure surface-atmosphere exchange fluxes of refractory BC (rBC) particle mass and number by eddy covariance. Dry deposition measurements are combined with established techniques for measuring BC in precipitation using the SP2, and compare the total deposition of BC by dry and wet pathways. We report field measurements of rBC dry and wet deposition rates during an initial deployment of the approach during summer 2017 at the US DOE Southern Great Plains site in Oklahoma, USA. We close with a discussion of potential applications of the approach for assessing BC deposition to different land surfaces, including snow and ice.

P1-12 Determination of mineral dust and elemental carbon in snow samples

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Mineral dust deposited on snow has a great impact on its chemical composition mainly increasing the alkalinity and the concentrations of Ca2+ and Mg2+. Besides, the albedo of snow surfaces featuring deposited mineral dust is decreased, leading to faster and earlier melt-off of the snow cover. Deposited elemental carbon (EC) has due to its blackish colour an even stronger albedo-reducing effect. Therefore it is of interest to determine the amount of both parameters, mineral dust and EC, in snow samples.

Here we evaluate a thermal-optical method for the combined determination of mineral dust and EC in snow samples within the same analytical run, thereby using carbonate carbon as proxy for mineral dust. Snow samples collected at the surrounding glaciers of the Sonnblick Observatory, located in the Austrian National Park Hohe Tauern in the Eastern Alps were used for analysis. It is well known that samples collected there regularly contain mineral dust (Greilinger et al., 2018).

Snow samples were taken annually after the winter accumulation period at maximum snow height. Thereby a vertical column of 20 cm increments down to the glacier ice is sampled. These samples were melted in a glass beaker, filtrated over prebaked quartz fibre filters and subsequently thermal-optically analysed (Sunset Lab. Instrument). This procedure is already described in literature for the determination of EC and water-insoluble organic carbon, though different thermal protocols are used (Pedersen et al., 2015; Voisin et al., 2012). Here we use and compare the applicability of the EUSAAR_2 and NIOSH870 temperature protocols for the parallel determination of EC and carbonate carbon.

The method characterization comprises factors like losses during melting, potential errors due to an inhomogeneous distribution on the filter, an evaluation of blanks, a comparison with filters fumigated with HCl, a comparison of carbonate carbon concentrations with Ca2+ concentrations determined via ion chromatography and a comparison with reference substances like CaCO3 and K2CO3.

References:

Greilinger, M., et al. (2018). Contribution of Saharan dust to ion deposition loads of high alpine snow packs in Austria (1987-2017). *Frontiers in Earth Science*, *6*, 126.

Pedersen, C. A., et al. (2015). In situ observations of black carbon in snow and the corresponding spectral surface albedo reduction. *Journal of Geophysical Research: Atmospheres*, 120(4), 1476-1489.

Voisin, D., et al. (2012). Carbonaceous species and humic like substances (HULIS) in Arctic snowpack during OASIS field campaign in Barrow. *Journal of Geophysical Research: Atmospheres*, *117*(D14).

P1-13 Analysis of highly loaded emission samples using a thermal-optical method- advantages of a manual evaluation method

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Carbonaceous compounds represent a major fraction of particulate matter. This holds true for ambient air samples, but is even more obvious when emission samples from residential wood combustion are evaluated. Still, a comprehensive chemical analysis of emission samples is necessary to determine emission factors, or to obtain source profiles which can later be used for source apportionment. Despite considerable adjustments quantification of highly loaded emission samples is still associated with considerable challenges, i.e. inhomogeneous contribution on filters or high filter loadings, which demand the analysis of small sample aliquots and may set additional limits to optical methods.

This study represents a manual quantification method for highly loaded emission samples from different firewood combustion devices. Sampling was divided into hot and cooled total suspended particle (TSP) samples. Sampling of hot flue gas was realized downstream the combustion chamber, while 'cooled-phase samples' were sampled after dilution with compressed air. Analysis of organic carbon (OC) and elemental carbon (EC) was performed in duplicates by an OCEC analyzer (Sunset Laboratory Inc.), applying the EUSAAR_2 protocol in the transmission mode. Generally different contributions of the carbonaceous aerosol fractions could be observed in the hot and cooled-phase samples. Hot-phase samples consist primarily of EC while OC was primarily quantified in cooled-phase samples. First the split point between OC and EC was conducted automatically. Using this method the uncertainty of EC concentrations was rather high, when the duplicate samples were compared. This effect, that was obviously driven by the small changes of the laser signal during the first part of the analysis, made a manual verification of the split-point necessary.

The calculation of the manual split-point is based on the calculation of the highest laser signal before it significantly decreases during the inert phase (He-phase) of quantification. Different to the automatic method, no defined time interval at the beginning of the analyses was set to determine the highest value of the laser signal. This manual evaluation reduces the methods uncertainty of EC measurement, which was based on replicate analysis of emission samples, significantly. Thus, filter loadings ranging up to 2059 μ g cm-2 of OC and 2571 μ g cm-2 for EC could be evaluated.

P1-14 Differences and analogies of structural changes of CAST soot and atmospheric aerosol samples during thermal-optical analyses

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Elemental Carbon (EC), Black Carbon (BC) and Organic Carbon (OC) are important components of the atmospheric aerosol because of their climatic and health effects. However, the correct determination of these components is not trivial. Results of different measurement techniques show differences by factors up to nine especially in the presence of Brown Carbon (BrC) (e.g. Reisinger et al., 2008; Hitzenberger et al., 2006; Wonaschütz et al., 2009).

During thermal-optical analyses of EC and OC, samples are heated stepwise first in an inert (He), then in an oxidizing (He+O2) atmosphere. The pyrolysis of the samples during the inert mode is corrected for optically, but uncertainties in the OC/EC split remain (Cheng et al., 2012). BrC and other water soluble organic carbons (WSOCs) are thought to bias the results of thermal-optical measurement techniques due to their high potential to pyrolyze during the inert heating procedure. Also the presence of certain metal salts influences the pyrolyzation of OC (Wang et al. 2010). Although there is consent about the confounding role of pyrolyzation, the concrete structural reorganizations of the material during thermal-optical analyses are not fully understood.

In the present study structural changes of soot produced with a miniCAST generator (Jing Technologies) as well as of atmospheric aerosol samples during two thermal-optical measurement protocols (NIOSH870, Birch and Cary, 1996 and EUSAAR2, Cavalli et al., 2010) are investigated. EC and OC are determined for all samples with a dual-optics OC/EC analyzer (Sunset Instruments Inc.), which is also used as an oven for the preparation of the heated samples. The heated samples are analyzed with Raman Spectroscopy, which is sensitive to the bonding types and the degree of structural ordering (i.e. the amount of aromatic rings) in carbonaceous materials (Ferrari and Robertson, 2000). The content of BrC is measured with the Integrating Sphere method (Wonaschütz et al., 2009) and back trajectories are calculated with HYSPLIT for the atmospheric aerosol samples.

Both, atmospheric aerosol samples and CAST samples, with a high amount of BrC show changes in the Raman spectra during the heating process in the OC/EC instrument. The extent of the changes, however, is different for the two measurement protocols. The increase of structural ordering due to heating is slightly less pronounced for the EUSAAR2 protocol with a lower maximum temperature in the inert phase.

P1-15 Evaluation of VOC denuder efficiency and positive artefact due to denuder breakthrough using TCA08

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Measurement of particulate organic carbon with quartz fiber filters is prone to positive and negative sampling artefacts. Positive artefact results from adsorption of organic gases onto the filter surface and depends on the face velocity, sampling duration and location and can easily contribute more than 50% to total organic carbon concentration. Different approaches have been used to minimize the adsorption artefact and to quantify its magnitude: such as the "two filters" approach (quartz behind quartz, QBQ; quartz behind Teflon, QBT); the "slicing filters" approach; and the use of denuders. For routine measurements in monitoring networks, the denuder is the only practical and realistic approach. Some organic gases can nevertheless penetrate through denuder, which is known as denuder breakthrough, leading to denuder efficiency (DE) lower than 100%.

The positive artefact and efficiency of activated carbon honeycomb denuders, used by total carbon analyzer TCA08 (Magee Scientific), were evaluated in terms of sample air residence time within denuder (by mounting different number of monolith denuders in series). Additionally, positive sampling artefact was tested for different collection times (from 20 minutes to 2 hours) and different face velocities. An effective procedure for denuder thermal regeneration was developed.

TCA08 provides high time resolution measurements of total carbon (TC) concentration based on thermal method. Two parallel flow channels with two chambers allow us to perform denuder efficiency test by installing quartz filter above stream divider and denuder above one of the analytical chambers. Denuder efficiency was determined by comparing carbon content collected on quartz filters in parallel chambers (with and without denuder).

Measured efficiencies of used and new denuders were in the range from 35 to 90 % at 175 ms residence time (1 denuder monolith). DE significantly increased for longer residence times (2 and 3 denuder monoliths in series), especially in the case of denuders with lower efficiencies (of a single monolith). High DE (around 90%) was measured after thermal regeneration of spent denuders. Positive artefacts at face velocity 57 cm/s were measured in the range from 1.2 to 7.9 μ gC/m3 with higher artefacts and lower DE measured at shorter sampling time. VOC breakthrough was < 100 ngC/cm2 for denuders with DE > 70% and from 100 - 300 ngC/cm2 for denuders with DE between 35 and 70%.

P1-16 FATCAT: a novel semi-continuous measurement system for the carbonaceous aerosol fraction

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Total aerosol carbon mass (TC) is a major constituent of the atmospheric fine aerosol particles. However, this fraction is not yet continuously monitored at atmospheric measurement stations. Adding a stand-alone TC measurement is thus crucial to complete the existing measurement program for a comprehensive interpretation of the impact of aerosols on our climate. Current standards based on mass concentration are also not enough to characterize aerosol particles in terms of their potential to cause adverse health effects. On the side of emission monitoring, European projects like the project Common European test method for the determination of particulate matter emissions (PME) of solid fuel burning appliances and boilers (EN-PME-TEST) have therefore reviewed the use of a metric based on TC instead of the total PME. This approach is mentioned as long-term because it appears promising and interesting but is not mature enough to be proposed as candidate method at a European level right now. One of the reasons is that there is no simple and robust measurement system for TC available commercially.

In order to fill this gap, we have developed the fast thermal carbon totalizator (FATCAT). FATCAT is a portable semi-online system for the determination of TC. Our device collects a sample and then heats it rapidly, within 50 seconds, to 800°C under an oxidizing atmosphere. Further oxidation of carbonaceous material is achieved by a catalyzer located downstream of the heating unit. TC detection is done by means of a CO_2 measurement. Fast heating allows for a short analysis cycle of

less than two minutes. The high dynamic range of the instrument, from a limit of detection $LoD=0.4 \mu g$ of carbon (μg -C) up to at least several hundreds of μg -C, and a sampling rate of up to one cubic meter per hour means that FATCAT can be used for monitoring ambient concentrations or as an emission measurement device. Sample collection time for ambient concentrations is typically between 30 minutes and one hour and can be as short as a few minutes for emission measurements. FATCAT shows a very good linearity when compared against commercial state of the art devices for synthetic carbonaceous aerosol samples and for emissions from biomass burning appliances.

Finally, we discuss an alternative metric for emission monitoring that incorporates recent scientific results and is compatible with type-approval testing as well as field measurements. This metric incorporates the potential formation of secondary organic aerosol by aging emissions in an oxidation flow reactor and quantify them using FATCAT.

This work has been supported by the Swiss Federal Office for the Environment and by METEOSwiss.

Further reading:

Keller, A., H. Burtscher: Characterizing particulate emissions from wood burning appliances including secondary organic aerosol formation potential, J. Aerosol Sci. **114**, 21-30, 2017.

P1-17 Method for off-line BC determination of filters of different station types in Austria using transmissometry

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Carbonaceous particles such as organic carbon, elemental carbon and carbonate are main constituents of ambient particulate matter (PM). Black carbon (BC) forms the absorbing fraction of these particles (Bond et al., 2013). BC, emitted into the atmosphere through incomplete combustion of fossil and biomass fuels, represents an important part of PM in urban areas and is associated with serious health effects. Its optical properties make it an important climate forcer. In many national ambient air quality networks no routine on-line BC measurements are performed, but routine collection of daily PM filter samples is implemented. These filters could be used for retrospective EC or BC determination using off-line instrumentation.

The reference method for the determination of elemental carbon (EC) and organic carbon on filters is the thermal-optical measurement with the EUSAAR2 temperature program (EN 16909:2017-06, 2017). This method is quite time consuming, and filters of materials other than quartz fiber cannot be measured directly. Routine monitoring of EC collected on filters of various materials in existing monitoring networks is ambitious. An alternative method, which would be easier to use and would require less funds, would provide the opportunity to perform comprehensive monitoring and obtain long-term time-series where archived also filters could be used. Based on Davy et al. (2017), we tested two approaches for the determination of BC via optical attenuation measurements with a transmissometer OT-21 (Magee Scientific) on quartz fiber filters from different station types (urban-traffic, rural-background and remote) within the Austrian air monitoring network. The data set comprises 299 filters, sampled for 24 h from midnight to midnight local time using High-Volume-Samplers. PM concentrations ranged from approximately 5-100 μ g m-3 and covered all seasons.

We present a comparison of the two different approaches as well as results for the observed filter loading parameter k and the mass attenuation cross section σ for station types ranging from urban to global background stations.

We show that the application of the transmissometer measurements provide a quick, easy and nondestructive quantification of BC on either fresh sampled or archived filters of different station types. If the station type is known and the respective k and σ values are used, the deviation between EC measured with the reference method and BC falls to or below 10%. Applying the method for stations not classified as urban, rural or remote, a deviation of values up to 23% can be expected. The optical analysis of filters allows users to obtain long-term time-series going back to times when no on-line instruments existed and to obtain these data for sites with no on-line instruments. As an example, we show the evaluation of weekly high-volume quartz fiber filters sampled over almost 2 years at the remote GAW station Hoher Sonnblick (3106 m a.s.l.) in Austria.

P1-18 Light Scattering and Extinction Measurements Combined with Laser-Induced Incandescence for the Real-Time Determination of Soot Mass Absorption Cross Section

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The aerosol albedometer was combined with laser-induced incandescence (LII) to achieve simultaneous measurements of aerosol scattering, extinction coefficient, and soot mass concentration. A colinear beam of both ? = 532 and 1064 nm laser light was used for experimentation. The green beam was used to perform cavity ring-down spectroscopy (CRDS), with simultaneous measurements of scattering coefficient made through use of a reciprocal sphere integrating nephelometer. The near IR (1064 nm) beam was spectrally selected and directed into a second integrating sphere and used for LII of light-absorbing kerosene lamp soot. Thermal denuder experiments showed the LII signals were not affected by the particle mixing state when laser peak power was 1.5 - 2.5 MW. The separate measurements of optical properties and soot mass concentration allowed determination of mass absorption cross section (M.A.C., m2/g) with 1 min time resolution when black carbon concentrations were in the low microgram per cubic meter range. Fresh soot from a kerosene lamp exhibited a mean M.A.C and standard deviation of $9.3 \pm$ 2.7 m2/g while limited measurements on dry ambient aerosol yielded an average of 8.2 ± 5.9 m2/g when soot was at concentrations > 0.25 μ g/m3. The combined method also detected increases in M.A.C. values associated with enhanced light absorption when polydisperse, laboratory-generated ns-soot particles were embedded within or coated with ammonium nitrate, ammonium sulfate, and glycerol. Glycerol coatings produced the largest fractional increase in M.A.C. (1.41-fold increase), while solid coatings of ammonium sulfate and ammonium nitrate produced increases of 1.10 and 1.06, respectively. Fresh, soot did not exhibit increased M.A.C. at high relative humidity (RH) presumably due to its hydrophobic nature; however, lab-generated soot coated with ammonium nitrate and held at 85% RH exhibited M.A.C. values nearly double the low-humidity case. The hybrid instrument for simultaneously tracking soot mass concentration and aerosol optical properties in real time is a valuable tool for probing enhanced absorption by soot at atmospherically relevant concentrations.

P1-19 Intercomparison of aerosol absorption photometers in one intercomparison workshop

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Monitoring of atmospheric pollutants such as black carbon is of interest for its impact on air quality and climate. Given its importance, measurements of black carbon must be conducted with instruments operating in optimal conditions to generate reliable and comparable spatial and temporal results. According to the WMO and GAW, performance checks, including inter-laboratory intercomparisons is one of the procedures for quality controls in measurements activities (WMO, 2016).

Considering to this necessity, networks such as ACTRIS (the European Research Infrastructure for the observation of Aerosol, Clouds and Trace Gases), carry out instrumental comparison and calibration workshops, where operators verify the status of their instruments and compare them with reference equipment to guarantee quality in long-term measurements, which allow identifying trends in global distributions of aerosols.

A intercomparison workshop for filter-based particle light absorption photometers was conducted in January 2019 with the objective of investigate the individual behavior of 17 instruments (AE33 aethalometers) and their comparability, which are operated by research institutions, universities or governmental entities in Europe. The methodology and preliminary results of the intercomparison are presented in this work. The instruments were compared with one reference set consisting of an Integrating Nephelometer (Ecotech Aurora 4000), a Multi-Angle Absorption Photometer (MAAP) and three extinction monitors (Cavity Attenuated Phase Shift extinction, CAPS PMex) used to measure the particle light scattering, backscattering, absorption and extinction coefficients. A flame-based BC diffusion generator (mini-CAST 5203C, Jing Ltd, Switzerland) was used to generate the synthetic measured particles in a controlled environment; ambient air concentrations were also measured.

During the deployment of the intercomparison, a variability smaller than 20% between the reference setup and the AE33 absorption photometers was observed. Similarly, the observed unit-to-unit variability showed some differences that are being evaluated currently. Both, the reference and unit-to-unit deviations are in some cases explained by the filter material, the total particles load in the filter, and the preliminary flow calibrations carried out with non-calibrated devices. The activity and preliminary results highlight the importance of careful calibration of flows and filter sampling spot sizes.

WMO. (2016). WMO/GAW Aerosol Measurement Procedures, Guidelines and Recommendations 2nd Edition. Switzerland: World Meteorological Organization & Global Atmosphere Watch.

P1-20 Collection of Black Carbon in a Particle-Into-Liquid Sampler

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Steam collection devices such as the Particle-Into-Liquid Sampler (PILS, Weber et al., 2001) produce liquid samples containing aerosol particles in solution or suspension. In common applications, the water-soluble particulate material is then analyzed, while the fate of water-insoluble components is often neglected. In this study (Wonaschuetz et al., 2018), we show that hydrophobic and insoluble soot particles from a CAST soot generator are sampled in detectable quantities by the PILS. The overall collection efficiency was found to be on the order of 20%. We conclude that the presence of hydrophobic particles in liquid samples from steam collection cannot always be neglected.

Weber, R. J., Sullivan, A. P., Peltier, R. E., Russell, A., Yan, B., Zheng, M., de Gouw, J., Warneke, C., Brock, C., Holloway, J. S., Atlas, E. L., Edgerton, E. (2001). A study of secondary organic aerosol formation in the anthropogenic-influenced southeastern United States. *J. Geophys. Res. 112*, D13, doi:10.1029/2007jd00840.

Wonaschuetz, A., Haller, T., Sommer, E., Witek, L., Grothe, H., Hitzenberger, R. (2018). Collection of soot particles into aqueous suspension using a particle-into-liquid sampler, *Aerosol Science and Technology*, doi: 10.1080/02786826.2018.1540859

P1-21 In situ absorption measurements with photothermal interferometry

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In situ photothermal methods investigate aerosol absorption without the complicating effects of deposition of particles onto a filter. These methods rely on the direct link between absorbed energy by the aerosol particles and heat transfer to the surrounding gas, which is typically measured as an induced pressure wave or a change in the gas refractive index. Instruments employing these methods can be highly accurate and precise and allow highly time resolved measurements of in-situ aerosol absorption by black carbon and other absorbing particles.

We report on our current instrument development of an instrument based on photothermal interferometry (PTI). As PTI can be calibrated with light absorbing gases, PTI can be used as a reference for aerosol light absorption from which Black Carbon mass concentration can be precisely inferred. This *in situ* absorption technique does not rely on resonant excitation for signal detection (Moosmüller *et al.* (1996), Sedlacek (2006)). With PTI, the local change of refractive index within the coincident volume of the excitation (pump) and detection (probe) beams, resulting from the absorption of light by aerosol particles and subsequent transfer of heat to the surrounding gas, is detected with an interferometer. As PTI is a non-resonant method, it is immune to the damping and non-linearities present in resonant photoacoustic instruments.

We are currently investigating whether PTI also suffers from the same reduction in signal for particles coated with volatile substances as other *in situ* methods. If the pump light intensity is too high, it is expected that the measured signals are impaired due to the latent heat consumption from the evaporation of the volatile substances from the aerosol particles. Since the time evolution of these evaporation and recondensation processes can be accessed with our PTI technique, these pump laser power induced artefacts can be characterized and minimized such that PTI is not restricted by such latent heat effects.

This work is supported by the Swiss National Science Foundation (Grant No 200021_172649) and the EMPIR Black Carbon project (Metrology for light absorption by atmospheric aerosols).

Moosmüller, H., Arnott W.P. (1996) *Optics Letters* **21**(6), 438-440. Sedlacek, A.J. (2006) *Rev. Sci. Instr.* **77**(6), 064903-1-064903-8.

P1-22 Assessing multi-spectral measurement methods for aerosol optical properties by closure experiments

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The quantification of the aerosol direct radiative effect on climate requires observational knowledge of the key aerosol optical parameters, including their wavelength dependence. In this work, we investigate a broad set of measurement techniques for extinction, scattering and absorption coefficients deploying various types of laboratory-generated aerosols, including ammonium sulfate, sodium chloride, PSL reference standards (polysterene latex beads), Cabot industrial soot and Aquadaq (colloidal graphite) as well as carbonaceous particles emitted by an inverted propane flame generator (Argonaut Scientific Corp., Edmonton, AL, Canada). Applied methods include an Integrating Nephelometer for wavelengths of 450, 550 and 700 nm (Model 3563, TSI Inc., St. Paul, MN, USA), a Tricolor Absorption Photometer with wavelengths of 467, 528 and 652 nm (TAP, Brechtel MFG, USA), two Cavity Attenuated Phase Shift Single- scattering Albedo monitors with 450 and 630 nm for extinction and scattering coefficient(CAPSssa, Aerodyne Research Inc., USA), a Multi Angle Absorption Photometer at 632 nm wavelength (MAAP, Thermo Scientific, USA), and an Optical Particle Counter (OPC 1.129, Grimm Aerosol Technik GmbH Co & KG Germany) for size distribution measurements from about 250 nm to 2.5 μm. Particle size distributions were also measured separately with a stepwise-operated combination of a DMA (5.400, Grimm Aerosol Technik GmbH Co & KG Germany) and CPC (5.411, Grimm Aerosol Technik GmbH Co & KG Germany) system.

The aerosol generation was designed to control load and single scattering albedo (SSA) of the sample aerosol by means of a Labview-based PID controller and diluter. The set-up provides stable conditions for generating aerosol samples at prescribed properties like SSA values ranging from 0.3 to 1.0, different levels of extinction, scattering and absorption coefficients, and Angstrom exponents.

For spherical light absorbing particles (Aquadaq), we found excellent agreement between the absorption coefficients deduced from extinction (CAPS) and scattering (Integrating Nephelometer) coefficients by the Differential Method for both in situ (CAPS SSA extinction minus CAPS SSA scattering) and filter-based (MAAP, TAP) techniques at 630 nm. For the other types of light absorbing particles like Cabot industrial soot and flame soot for rich combustion (low C/O ratio), we found deviations of up to 30% in both directions. For flame soot from lean combustion (high C/O ratio), the deviations increase, particularly for the blue channel.

We will present the results from the different closure studies and discuss the accuracy of applied techniques. Particular focus will be put on the potential impact of organic carbon compounds from unburned hydrocarbons which may absorb strongly in the blue and thus modify the light absorption properties of the flame soot significantly.

P1-23 Measurement of Aircraft Engine Soot Emissions Using the ESCOM

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The International Civil Aviation Organization (ICAO) has set emissions standards for non-volatile PM (nvPM) emissions, primarily light absorbing carbon, from aircraft engines. It relies on the SAE E-31 Committee to draw up specific technical standards for the measurement of these emissions as well as certification procedures for nvPM emission monitors. Currently, two instruments have been certified as meeting the committee's criteria - one utilizes photoacoustic absorption spectroscopy and the other laser induced incandescence. In order to meet the need for another measurement approach, Aerodyne Research is developing the Engine Soot Compliance Monitor (**ESCOM**) based on its CAPS PMssa monitor.

CAPS PMssa monitors provide simultaneous measurement of both particle extinction and scattering on the same sample volume (and thus particle absorption) with great sensitivity (0.1 ug m-3) and accuracy. The mass concentration of nvPM is obtained by dividing the measured absorption by a representative mass absorption coefficient (MAC), such as for mature soot. This approach offers the potential for being based on an absolute particle standard rather than a comparison to the Sunset Laboratory OC/EC Analyzer (the current standard). The **ESCOM**, which combines an internal carbon dioxide sensor with the CAPS PMssa, provides a real time measurement of the nvPM emission index (a measure of the amount of nvPM emitted per kg of fuel expended) if the chemical composition of the fuel is known.

We will present results from the EPA-sponsored VARIAnT2 and NASA/DLR-sponsored ND-MAX campaigns which involved measurements of nvPM emissions from a test-bed mounted engine and from an Airbus A320, respectively, using a version of the monitor which operates at 630 nm. These tests involved various types of biofuel mixtures as well as standard jet fuel. We will also describe a new version, which operates at 780 nm, thus avoiding an interference posed by high concentrations of nitrogen dioxide in engine emissions. Results from our new ESCOM instrument, collected during the EPA-sponsored VARIAnT4 campaign which included calibration and certification tests, will be shown as well.

P1-24 Photophoresis used for measurements of light absorption by a single particle

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The surface of an illuminated, light absorbing particle is, most likely, unevenly heated relative to its surrounding. The temperature difference between the illuminated and the 'dark' side of the particle results in an uneven momentum transfer from colliding gas phase molecules. This leads to a net photophoretic force (Fph) acting on the particle in the direction of the momentum transfer gradient that is related to its complex refractive index (RI) and to its size parameter through the irradiant internal fields. As such, it may lead to a net force away from (positive) or towards (negative) the light source. Here, we report on preliminary results of using this phenomenon to quantify light absorption by a single particle levitated in an electrodynamic balance (EDB) with imaginary part of the complex RI in the range of 10-5 to 10-3. An advantage of the EDB is that heterogeneous chemistry and photochemistry experiments, on a single particle, are performed with realistic atmospheric gas concentration and aging time. In such experiments, continues or occasional probing of the particle's light absorption by ageing or secondary organic aerosols.

Posters 2

2.3 Source characterization and source apportionment

P2-1 Studies of carbonaceous particles at a traffic site -Moscavide/Lisbon, Portugal

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Particulate matter (PM) is a complex mixture of extremely small particles and liquid droplets emitted by different sources and produced in the atmosphere. It is very spatially and temporally heterogeneous and many sources contribute to PM and their gaseous precursors. One of the most important fractions is carbonaceous matter, which includes a refractive primary component - black carbon (BC).

BC is emitted during the incomplete combustion of fossil fuels, biofuels, and biomass burning and absorbs at all wavelengths of solar radiation. Together with methane and tropospheric ozone, BC is one of the most important contributor to current global warming after carbon dioxide. BC and co-pollutants are currently considered a major environmental cause of respiratory and cardiovascular diseases, with a global estimation of more than 7 million premature deaths annually from exposure to indoor and outdoor polluted air. Thus, it is of main importance to determine the chemical composition of submicron aerosol at high time resolution, providing the necessary information for accurate source apportionment.

With the purpose of characterising ambient aerosols and their time evolution and to assess the contribution of the main emission sources and processes leading to aerosol formation in the atmosphere a campaign was conducted in the urban centre of Moscavide (North of Lisbon, Portugal). A traffic air quality monitoring station was located close to one-way street with a total length of 1.2 km. Particulate matter was sampled and on-line BC measurements (Aethalometer AE33) and total carbon (TC, measured by TCA08) were performed simultaneously. The sampled filters were analysed by gravimetry, by XRF, for the determination of element concentrations, and by thermo-optical analysis, for the measurement of organic and elemental carbon.

We present highly time resolved measurements, perform source apportionment and investigate local and regional pollution events. Separation of contributions to BC from different combustion sources is based on the dependence of absorption on the wavelength, while the measurement of TC allows the determination of equivalent OC, that is the difference between TC and EC (inferred from BC), at high time resolution. The combination of the data generated by the on-line equipments was combined with data from the chemical analysis of filters (OC/EC and elements), obtaining for the first time the parameters for the thermal protocol applied in the University of Aveiro. Additionally, data from chemical characterisation of particles is used to support the source apportionment.

Acknowledgements

The authors wish to thank Life Program - Life Index Air project, Interreg Med – REMEDIO project, Cost Action - CA16109 COLOSSAL.

P2-2 Apportionment of the particulate carbonaceous fraction by Ionic and Mass Balance (IMB) in a traffic influenced urban atmosphere in Portugal

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The IMB source apportionment method previously developed for particulate matter (PM) contamination in a background marine dusty atmosphere (Cardoso et al., 2018) was adapted for application in an urban atmosphere containing large amounts of carbonaceous PM. PM2.5 and PM10 aerosol samples, collected at a traffic site during for one year in Porto, Portugal, within the AIRUSE project, and analysed for OC, EC, levoglucosan, ions and trace elements, were used to test the methodology.

The IMB method relies on ionic and mass balances and on the use of edge lines between analysed species, associated with bibliographic information, to, totally, apportion the measured PM mass. Here we detail the carbonaceous aerosol component.

From the Al/Fe edge line, the amount of Fenex, originated from non-exhaust traffic, was estimated. The edge line between Fenex and EC was used to calculate ECnex emitted from the same non-exhaust road traffic source. Edge lines between the remaining EC, (EC-ECnex), or OC, and levoglucosan permitted the determination of biomass burning carbonaceous emissions (ECbb and OCbb). The edge line between the remaining OC (OC-OCbb) and EC (EC-ECnex-ECbb) was used to estimate secondary OCsec and traffic exhaust primary carbonaceous matter (OCtraf, ECtraf). The observed edge lines compared very favourably with ratios in emission sources taken from bibliography.

Ten sources/formation processes were estimated with the adapted IMB methodology, accounting for, on average, 85% of the measured total mass concentration. Based on bibliographic and thermodynamic information, water was added to water soluble and hygroscopic source components, bringing the PM coverage to approximately 100%. The IMB methodology was compared with Positive Matrix Factorization (PMF) applied to the same samples (Amato et al., 2016), showing comparable results, principally in what refers to the carbonaceous fraction. In summer, secondary organic matter, together with secondary inorganic aerosol formation, dominated PM2.5 and PM10. In winter, there was an important contribution of biomass burning to the measured PM.

References

Cardoso J., Almeida S.M., Nunes T., Almeida-Silva M., Cerqueira M., Alves C., Rocha F., Chaves P., Reis M., Salvador P., Artiñano B., Pio C. (2018) Source apportionment of atmospheric aerosol in a marine dusty environment by Ionic/composition Mass Balance (IMB). Atmospheric Chemistry and Physics, 18, 13215-13230.

Amato F., Alastuey A., Karanasiou A., Lucarelli F., Nava S., Calzolai G., Severi M., Becagli S., Gianelle V.L., Colombi C., Alves C., Custódio D., Nunes T., Cerqueira M., Pio C., Eleftheriadis K., Diapouli E., Reche C., Minguillón M.C., Manousakas M., Maggos T., Vratolis S., Harrison R.H., Querol X. (2016) AIRUSE-LIFE+: a harmonized PM speciation and source apportionment in 5 Southern European cities. Atmospheric Chemistry and Physics. 16, 3289-3309.

P2-3 Emissions of black carbon in a road tunnel

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A sampling campaign was carried out in the Liberdade Avenue tunnel (Braga, Portugal) to monitor black carbon (eBC-equivalent black carbon) by means of an Aethalometer AE-31, and gaseous pollutants (CO2, CO, NOx). Traffic volume by vehicle category through the tunnel was counted manually. Simultaneous measurements were conducted in an urban background site in the vicinity. Inside the tunnel, the mean eBC mass concentration was 23±11 µg m-3, reaching a maximum hourly value of 50±8 µg m-3. Peak concentrations on weekdays occurred between 1400 and 1900 UTC, during the rush hours, when large numbers of people are travelling to or from work or school. However, on weekends, a peak between 1000 and 1200 UTC was observed, probably due to commuting to shopping and leisure activities. A mean Absorption Angström Exponent (AAE470-950nm) value of 0.77±0.05 was obtained. Positive significant correlations were observed between eBC and the number of light vehicles (r=0.47; p<0.001) and between eBC and the gaseous emissions: CO (r=0.67; p<0.001), CO2 (r=0.72; p<0.001), NO (r=0.65; p=0.007) and NO2 (r=0.73; p<0.001). The contribution from fossil fuel (eBCff) and biomass burning (eBCbb) was estimated through the Aethalometer Model (Sandradewi et al., 2008). eBCff was 23.2±11.4 µg m-3 (about 99% of total eBC), while eBCbb was 0.2±0.5 µg m-3, showing a residual penetration of eBC into the tunnel from residential biomass combustion emissions in the city. The mean black carbon emission (EFBC) estimated to be 0.34±0.08 g (kg factors were fuel)-1 and 0.13±0.08 mg veh-1 km-1, which are higher than those derived in other studies for gasoline and diesel vehicles in road tunnels.

The study of black carbon in road tunnels contributes to better characterise emissions of this pollutant from traffic in real circulation conditions and without influence from other sources, providing information on BC emission factors, which are useful as input data to climate and air quality models, as well as to updated emission inventories.

Sandradewi et al., 2008. Using aerosol light abosrption measurements for the quantitative determination of wood burning and traffic emission contribution to particulate matter. Environ. Sci. Technol. 42, 3316–3323.

P2-4 Impacts of engine regime and fuel type on the chemical composition of soot particles in gasoline and diesel vehicle emissions

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Vehicle particle emissions are a major public health problem, especially in urban environments subjected to dense traffic [1]. The use in the vehicle engines of pure biofuels or blends with traditional fossil fuels induces effects that are still poorly known on the chemical composition of the particles emitted in the exhaust.

As part of the BIOTOX project, the chemical composition of particles emitted by gasoline (Ecoboost 1.0 direct injection gasoline engine (DISI) in a Ford Focus and 1.4 multi-point injection (MPI) engine in a Škoda Fabia) or heavy-duty diesel (Iveco Tector) engines was analyzed according to the nature of these new fuels (pure fossil fuels or mixed with biofuels) and the engine regime. The soot particles, deposited on quartz fiber filters, were chemically characterized using mass spectrometry techniques: two-step laser mass spectrometry (L2MS) with different one-photon (SPI) or two-photon resonant (R2PI) ionization schemes, and secondary ionization mass spectrometry (SIMS). These measurements give access to the individual chemical species adsorbed on the particles. They were supported by thermo-optical analysis, capillary electrophoresis, and FTIR spectroscopy, providing additional information about the content in organic carbon (OC) and in elemental carbon (EC), the concentration of water-soluble ions, and functional groups characterizing the particle emissions, respectively.

Associating individual molecules or their fragments detected by mass spectrometry with chemical functionalities determined by FTIR remains a delicate task. To facilitate this work, principal component analysis (PCA) and hierarchical clustering (HC) were applied to all the mass spectra in order to identify families of species from the same sources of combustion. Specific markers of the fuel used could also be determined. Major differences in the chemical composition between the particle emissions from gasoline and diesel engines will be outlined as well.

This work was supported by the Czech Science Foundation, the Russian Foundation for Basic Research, the Labex CaPPA, and the CPER CLIMIBIO.

[1] H. Libalova, P. Rossner, K. Vrbova, T. Brzicova, J. Sikorova, M. Vojtisek-Lom, V. Berenk, J. Klem, M. Ciganek, J. Neca, K. Pencikova, M. Machala et J. Topinka (2016). Comparative analysis of toxic response of organic extracts from diesel and selected alternative fuels engine emissions in human lung BEAS-2B cells. *Int. J. Mol. Sci.* 17: 1–24

[2] O. B. Popovicheva, C. Irimiea, Y. Carpentier, I. K. Ortega, E. D. Kireeva, N. K. Shonija, J. Schwarz, M. Vojtíšek-Lom et C. Focsa (2017). Chemical Composition of Diesel/Biodiesel Particulate Exhaust by FTIR Spectroscopy and Mass Spectrometry: Impact of Fuel and Driving Cycle, *Aerosol Air Qual. Res.* 17 (7), 1717–1734

P2-5 Analyzing Carbonaceous Particles from Paving Emissions

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Mastic asphalt (MA) is an important construction material mainly used for infrastructure pavements as well as industrial and garage floors. As mastic asphalt construction sites are often limited in space, the prevalent form of construction is by manual paving. Therefore, the emissions caused by mastic asphalt are not only relevant for the environment, but also highly relevant for workers' health. In this study, we examine four mastic asphalt mixtures in terms of their emissions and worker exposure at various construction temperatures, ranging from 195 °C to 245 °C. We conducted three laboratory studies and a field study to evaluate the emissions away from the construction site, emissions in close proximity to the construction site, direct worker exposure and, for the very first time, also the absolute emissions in mass PM10 a.d. per mass of MA. The experiments show that a big part (80 wt%) of the PM10 a.d. emissions consists of particles smaller than 0.8 μ m a.d. and are therefore very health relevant. Furthermore, we could show consistently in all our experiments that decreasing the paving temperature by 50 °C (by using a MA mixture workable below 200 °C) leads to an emission reduction of up to 70%.

Weiss, F., et al. Reducing paving emissions and workers' exposure using novel mastic asphalt mixtures, Building and Envrionment, 137, 51-57, 2018.

P2-6 PM characterization in barbecue restaurants

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Grill/barbecue restaurants are very common in Portugal, often with a barbecue area open to the customers room. Most grill and barbeque appliances are operated with vegetable charcoal, which is a strong source of many pollutants, mainly particulate matter (PM). In order to assess and characterise the indoor air quality in these type of spaces, a survey of 2 weeks was performed in 3 restaurants in the Aveiro city that use charcoal. All the restaurants cooked fish and meat barbecued/grilled meals, and two of them are as well a take away service. In these two restaurants barbecue chicken is the main product.

Continuous recording of comfort parameters (temperature, relative humidity and light) and indoor pollutants (CO2, CO, NO2, TVOCs and PM1, PM2,5, PM4 and PM10) was performed, using portable equipment (GrayWolf and DustTrak TM II Aerosol Monitor 8530). Exposure assessment was carried out on one worker at each restaurant. A complementary gravimetric method was used, indoors and outdoors, only during the activity period, to quantify PM10 total mass concentrations with an Echo-Tecora sampling equipment (quartz filters) in agreement with the reference method (EN 12341). Organic (OC) and elemental carbon (EC) in particles were then analysed by a thermo-optical method. Pre-backed quartz filters were used to reduce the carbon blank values.

Lunch and dinner times always showed peak concentrations of all pollutants, most of them coinciding with the intensification of charcoal barbecue combustion. The indoor protection limit (8 h average) for PM10 (50 μ g m-3) was exceeded in all restaurants, while the threshold for CO (9 ppm) was surpassed in only one restaurant (Ordinance n.° 353-A/2013).

A good linear correlation was obtained between the PM10 gravimetric method and the continuous measurements with the DustTrak monitor (PMDustTrak = 0.93 PMgravimetric + 13.3, R2= 0.87). During the activity period (10 h – 22 h), the contribution of fine particles < 1 μ m to PM10 was >50%, attaining percentages larger than 80% most of the time. Frequently PM10 concentrations above 400 μ g m-3 were observed, with maxima that hit 1300 μ g m-3. Indoor PM10 was always higher than indoor concentrations, with an average ratio PMin/PMout close to 3. The in/out ratio of total carbon (TC) was slightly lower, denoting a greater contribution of indoor sources of inorganic particles. The carbonaceous fractions of PM10 were dominated by organic carbon, with OC/EC indoor ratios ranging 3 to 16, whilst the OC/EC outdoors varied between 3 and 7.

P2-7 Carbonaceous particles of small-scale gas flaring

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Assessments of harmful pollution in regions of intensive gas flaring is remaining to be one of the key objective of the current research over the world. In Gas Flaring Characterization campaigns environmentally-dangerous particulate emission is generated by laboratory jet diffusion flame which approaches the scale of a small industrial flare. A broad suite of physical, chemical, and microscopic techniques characterize the particulate emission properties obtained in a range of realworld gas flaring conditions and low hydrogen flare gas mixture (N2, CO2, C1–C4 hydrocarbons). Particle morphology is characterized by soot agglomerates composed from small size primary particles of graphitic disorder as internal structure. Microstructure reveals the dominant grouping of elemental carbon vs oxidized and mixed soot with metal impurities, well in accordance with high EC/OC ratio in bulk composition. Functionalized structure present alkanes and aromatics with oxygenated compounds. Simulations of practices of flaring of high hydrogen gas mixture (C1-C7) with water salt solutions exhibit the effects of entrained aerosols on nanostructure and chemical composition of emission in the upstream oil and gas industry. Intercomparison of gas flaring carbonaceous particles is presented in the view of other kind of combustion process with respect to temperature and fuel such as diesel emission and biomass flaming/smoldering.Assessments of harmful pollution in regions of intensive gas flaring is remaining to be one of the key objective of the current research over the world. In Gas Flaring Characterization campaigns environmentallydangerous particulate emission is generated by laboratory jet diffusion flame which approaches the scale of a small industrial flare. A broad suite of physical, chemical, and microscopic techniques characterize the particulate emission properties obtained in a range of real-world gas flaring conditions and low hydrogen flare gas mixture (N2, CO2, C1-C4 hydrocarbons). Particle morphology is characterized by soot agglomerates composed from small size primary particles of graphitic disorder as internal structure. Microstructure reveals the dominant grouping of elemental carbon vs oxidized and mixed soot with metal impurities, well in accordance with high EC/OC ratio in bulk composition. Functionalized structure present alkanes and aromatics with oxygenated compounds. Simulations of practices of flaring of high hydrogen gas mixture (C1-C7) with water salt solutions exhibit the effects of entrained aerosols on nanostructure and chemical composition of emission in the upstream oil and gas industry. Intercomparison of gas flaring carbonaceous particles is presented in the view of other kind of combustion process with respect to temperature and fuel such as diesel emission and biomass flaming/smoldering.

P2-8 Source Apportionment of Ambient Carbonaceous Aerosol in Ireland Using a Variety of Analytical Techniques

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As part of the EMEP/ACTRIS/COLOSSAL Winter Campaign (2017 – 2018), 150 PM2.5 filter samples were collected at four sites across Ireland; Carnsore Point, Co. Wexford, Mace Head, Co. Galway, Malin Head, Co. Donegal and on the campus of University College Dublin, all either rural or urban background sites, covering the four corners of the country. An AE33 multi-wavelength aethalometer was deployed at each site. Filter collections of PM for further offline analysis were made with a DIGITEL DHA-80 High Volume Sampler or a Partisol 2025i Sequential Air Sampler.

The aethalometer model was employed for apportioning biomass burning and fossil fuel combustion black carbon. Using source specific Ångström exponent values of 0.9 and 1.68 for α TR and α WB, respectively [Zotter *et al.*, 2017], initial results from the AE33 aethalometer show a strong diurnal trend. A traffic-related peak in black carbon levels is observed during morning rush hour in Dublin, while the evening peaks are dominated by domestic solid fuel burning emissions at all sites, with the exception of Mace Head which is extremely remote. Previous studies have noted the strong correlation between black carbon originating from wood burning (BCWB) and levoglucosan concentrations, which is a wood burning marker compound [Fuller *et al.*, 2014, Martinsson *et al.*, 2017]. The results from this campaign will be used to investigate this relationship further.

A portion of each filter was reserved for thermal-optical organic carbon/elemental carbon (OC/EC) analysis using the EUSAAR_2 protocol and the Sunset Laboratories OC-EC aerosol analyzer. The data processing employed the Attenuation Versus Evolved Carbon (AVEC) plot approach developed by Nicolosi *et al.*, 2018. The AVEC plots show the OC and EC content on each filter, and also enable quantification of pyrolysed carbon. The elemental carbon (EC) fraction derived from these measurements was subsequently compared to the BC measurements from the aethalometer at 880 nm and the levoglucosan content determined by GC-MS.

P2-9 Source apportionment of atmospheric carbonaceous aerosols collected in Krakow, based on concentrations of organic/elemental carbon (OC/EC) and carbohydrates

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Keywords: particulate matter, source apportionment, combustion, OC/EC, carbohydrates

Air pollution is nowadays a growing problem of global significance, mainly due to adverse health effects such as cancer, asthma, allergies or cardiovascular diseases. Especially large urban centres are heavily affected by deterioration of air quality. Atmospheric aerosol particles consist of both organic and inorganic compounds as well as materials of biogenic origin. Airborne particulate matter (PM) is emitted by numerous sources, most of them related to anthropogenic activities such as coal or biomass combustion in heat generation processes, gasoline and diesel combustion in car engines, and uncontrolled burning of solid wastes.

The study was focusing on determination of chemical composition of atmospheric aerosols collected in Krakow, Poland, from 23th Jan. 2018 to 12nd Sep. 2018 in order to obtain information on their sources. Altogether 294 samples were collected on quartz fibre filters. They represent PM10 and PM1 fractions collected with 24 h resolution. The analytical work comprised thermo-optical carbon analysis (Sunset OC/EC Lab Analyser), determination of 14 carbohydrates by means of High-Performance Anion-Exchange chromatography with Pulsed Amperometric Detection (ICS 3000, Dionex).

The highest mean concentration among carbohydrates was detected for Levoglucosan (0.21 µg/m3) which is well-known marker of biomass burning. Existence of numerous sources of carbonaceous aerosols in the city atmosphere (e.g. combustion, traffic) is reflected in highly variable OC/EC ratios. The mean OC/EC ratio for PM10 faction was equal 5.6 (range 2.2-17.3) to be compared with 5.1 (range 1.6-13.3) for PM1 fraction. Furthermore, the concentration of the inorganic anions and cations (Br-, NO3-, NO2-, F-, SO42-, PO43-, Cl-, Li+, Na+, NH4+, Mg2+, K+, Ca2+) were determined with isocratic ion chromatography on an ICS-1100 instrument (Thermo Scientific). Parallel to filter sampling on-line characterization with ACSM (Aerosol Chemical Speciation Monitor) and aethalometer was performed.

Acknowledgement

This article is based upon work from COST Action COLOSSAL supported by COST (European Cooperation in Science and Technology).

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P2-10 Variability and Source Apportionment of Equivalent Black Carbon (EBC) at a Regional Background Site in Central Europe

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Black carbon (BC) is a primary carbonaceous aerosol and is recognized to play an important role on public health and the Earth's climate system. The wavelength dependence of light absorption has been widely used to investigate the influence of fossil fuel (traffic emissions) and wood smoke in ambient air. There is a clear need for conducting studies using real-time BC measurements in Eastern Central Europe. This study focuses on a 5 year measurement of equivalent BC (EBC) at a Central Europe regional background site. Our aim is to identify the potential sources of EBC, especially the influence from fossil fuel and biomass burning.

The EBC in PM_{10} was monitored from September 2012 to December 2017 at the rural background NAOK (National Atmospheric Observatory Košetice, 49°35' N, 15°05' E), central Czech Republic. The measurements were performed at 4 m above the ground using a 7-wavelength aethalometer (AE31, Magee Scientific). The EBC data have been corrected for loading effect and the aethalometer model has been used to estimate the contribution from biomass burning and fossil fuel.

The results show a clear seasonal trend of EBC concentrations with higher values during winter $(1.00 \pm 0.87 \ \mu g \ m^{-3})$ and lower values during summer $(0.44 \pm 0.29 \ \mu g \ m^{-3})$. The concentration of EBC_{bb} (EBC from biomass burning) was much higher in winter $(0.39 \pm 0.31 \ \mu g \ m^{-3})$ than in summer $(0.07 \pm 0.11 \ \mu g \ m^{-3})$. In winter, the higher contribution from biomass burning (34.8 ± 17.1% to 42.5 ± 15.3% of total EBC) is consistent with the higher Delta-C (proxy for biomass burning) compared to summer when fossil fuel is the main source of EBC (97.4 ± 6.1%). Angstroem coefficient (α) value (1.1 ± 0.2) in summer is consistent with reported number for traffic emissions while in winter, increased emissions from biomass burning lead to a higher α -value (1.5 ± 0.2). This result is also in agreement with the strong correlation obtained between EBC_{bb} and biomass burning tracers (levoglucosan and mannosan) in winter when a Levo/Man ratio of 4.8 ± 0.7 was measured, consistent with reported values for softwoods burning.

The EBC diurnal pattern displays a typical morning peak that could be attributed to the morning traffic rush hour, as the EBC_{ff} (EBC from traffic) peak corresponds well to the other combustion-related elements behavior (NO_x, NO₂, SO₂ and CO). The concentrations of EBC reached a maximum in the evening, especially during winter that could be attributed to the increasing contribution of EBC_{bb} consistent with maximum Delta-C at this time. The diurnal profile suggests a reduced emission of EBC_{ff} from traffic during the weekend due to lower commuting, typical in the area. On the contrary, the contribution of EBC_{bb} is slightly higher during the weekend due to the increased operation of domestic heating devices (woodstoves / heating system). The location of local and distant sources of EBC_{bb} and EBC_{ff} has been investigated using the Conditional Probability Function (CPF).
P2-11 Retrieving information on black and brown carbon emission sources exploiting aerosol optical properties in an advanced receptor model

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Light absorption by the ensemble of atmospheric particles is estimated through the aerosol absorption coefficient bap. Among aerosol components, the fraction of carbonaceous aerosol known as black carbon (BC) is considered the main responsible for light absorption in the atmosphere. One peculiar feature of BC is a wavelength-independent imaginary part of the refractive index over the visible and near-visible regions. Recently, literature studies focused on brown carbon (BrC), light-absorbing organic matter with increasing absorption towards lower wavelengths, especially in the UV region.

In this work, a multi-wavelength measurement of bap (at λ =405 nm, 532 nm, 635 nm and 780 nm) on filter samples collected in Milan (Italy) in 2016 at different time resolutions (1 hour, 12 hours and 24 hours) was performed by our home-made polar photometer PP_UniMI[1,2,3]. This piece of information, together with the chemical speciation of the samples themselves, was exploited as input data in an advanced receptor model that is the multi-time model[4,5,6]. This modelling approach allows to use each experimental data in its original time schedule, avoiding the need to average high time resolution data over the longest sampling interval. Nevertheless, source apportionment studies carried out by multi-time model are still scarce in the literature and none of them has investigated the feasibility of introducing aerosol optical absorption properties yet.

Information about the Ångström Absorption Exponent (α) of BC and BrC emission sources and an estimate of the Mass Absorption Coefficient (MAC) of BC were retrieved as model outputs and they were found to be compatible with literature values. Knowledge of the atmospheric value of the Ångström Absorption Exponent of sources is particularly important, since existing source apportionment optical models (i.e. the widespread Aethalometer model[7]and the more recent Multi-Wavelength Absorption Analyzer - MWAA - model[8,9]) need a priori assumption on this parameter. Moreover, coupling optical and chemical information strengthened the identification of BC and BrC emission sources such as traffic and biomass burning; this can be particularly useful in receptor modelling when important chemical tracers (e.g. EC, levoglucosan) are not available.

- [1] Vecchi et al., 2014. J. Aerosol. Sci. 70, 15-25
- [2] Bernardoni et al., 2017a. J. Aerosol. Sci. 107, 84-93
- [3] Vecchi et al., 2019. This conference.
- [4] Zhou et al., 2004. Atmos. Environ. 38, 4909-4920
- [5] Ogulei et al., 2005. Atmos. Environ. 39, 3751-3762
- [6] Crespi et al., 2016. Sci. Total Environ. 541, 502-511
- [7] Sandradewi et al., 2008. Environ. Sci. Technol. 42:3316-3323
- [8] Massabò et al., 2015. Atmos. Environ. 108 1-12
- [9] Bernardoni et al., 2017b. Atmosphere 8, 218

P2-12 Characterization and source apportionment of air particulate matter in Bali, Indonesia

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Bali is famous among the tourists from all around the world due to its natural beauty as well as the culture and its highly developed arts. As much as 80% of Bali's overall economy may now depend on tourism. Tourism activities will impact on environment quality since it can cause the same forms of pollution as any other industry. Monitoring of air quality has been conducted since 2012. This study presents characterization and source apportionment of air particulate matter (PM) that obtained from long term monitoring in Denpasar as the capital city of Bali during 2012-2017. PM samples were collected once a week using a Gent stacked filter unit sampler capable for collecting particulate matter in the fine (PM2.5) and coarse (PM2.5-10) size fractions. Black carbon (BC) that is considered to be the second strongest contributor to global warming next to CO2 was also measured using an EEL smoke stain reflectometer. Chemical composition of PM was determined using ED-XRF. The PM data set including BC and major elements (Na, Mg, Al, Si, Fe, Zn, Ni, Cu, V, S, Pb, Cr, K, Ca and Ti) was analyzed using EPA-PMF (Positive Matrix Factorization) for source apportionment. The average of BC for fine fraction in Denpasar, Bali during the study period was 2.76±1.01 µg/m3. The ratio of the 24-hr BC concentration compared to the PM2.5 concentrations showed that BC comprises about 23.4% of the fine particulate matter collected at the sites. The source apportionment identified 6 factors i.e., biomass burning, sea salt, vehicles, soil, road dust and secondary S.

P2-13 Emission factor of PM0.1 related to light absorption carbon from biomass combustion in Thailand

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The direct combustion of biomass fuel dominates the utilisation of biomass fuels and is most important to environmental contamination study. Emission Inventory (EI) of particulate matter (PM) especially, the PM0.1, or nanoparticle from solid biomass burning have not been study so far in Asian countries. The shortage of corresponding Emission Factor (EF) would lead to huge uncertainty of EI. In this study, solid biomass fuel was investigated. The solid biomass burned in a horizontal tube furnace with an inserted quartz column. The PM was sampling using a cascade air samplers (Nano-sampler) for nanoparticles. This air sampler is based on inertial filter technology, which operates air inlet of the Nano-sampler is 40 L/min. PM0.1 of EFs from the burning experiment was calculate based on the flow rate of the Nano-sampler and particulate matter concentrations. Furthermore, the carbonaceous aerosols namely, black carbon (BC) and brown carbon (BrC) were also investigated by the optical integrating sphere (IS) method. The results displayed that EFs values for six types of solid biomass burning in the laboratory experiment range from 0.11 to 0.22 g/kg. The highest EFs come from Bagasse (0.22 g/kg), the minimum EFs derive from rice straw and sugarcane leave (0.11 g/kg). The BrC EFs are higher than BC EFs in PM0.1 for solid biomass burning. The EFs is significant to the development of strategies for pollution control and decrease the biomass burning.

P2-14 Chemical Composition and Source Identification of PM2.5 in Makassar City, Indonesia

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Airborne particulate matter samples (PM2.5 fine fractions and PM2.5-10 coarse fraction) were collected once a week from October 2012 to December 2017 using a Gent stacked filter unit sampler in Makassar, Indonesia. Makassar is the capital city of South Sulawesi Province, Indonesia, which is the largest city in the Eastern Indonesia. The mass concentration of PM2.5 and PM10 ranged from 3.61-37.8 and 4.98-80.7 mg/m3, respectively. These values were still below the daily limit of the Indonesian national ambient air quality standard for PM2.5 and PM10 (65 and 150 µg/m3, respectively). The annual average of PM2.5 and PM10 in Makassar were 12.56 and 17.61 mg/m3, respectively, Black carbon concentrations in the fine fraction PM2.5 were determined using smoke stain reflectometer. The annual average of BC concentration was 3.06 mg/m3 which contributes 26.5% of mass concentrations. Chemical composition were characterized using ED-XRF Epsilon 5 and identified several key elements such as Na, Mg, Al, Si, S, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb and As. Source identification using Positive Matrix Factorization (PMF) identified six factors for fine fractions. The identified sources are biomass burning, road dust, industry, vehicles, oil combustion and construction. The PMF results showed that vehicles and oil combustion were the major sources contributing to the PM2.5 mass in Makassar.

2.4 Aerosol concentrations, trends and transport – measurements and models

P2-15 Direct measurements of light absorbing particles impacts and ice nucleation activity in Svítnafelljökull

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Surface snow measurements of light absorbing particles were carried out in the spring at Svínafelljökull, an outlet glacier of the Vatnajökull Ice Cap (VIC) in southeast Iceland. The average annual rate of mass change of VIC (-1.34 ± 0.12 m w.e. a-1), during the period of 2002-2010, is one of the most negative mass balance values recorded in the 21 st century globally. The Svínafelljökull has retreated 800m and lost 30% of its 1890 volume. Light-absorbing particles, such as black carbon (BC), dust and brown carbon (BrC), alter the optical properties and melt of snow. This impact on snow reflectivity decline can be a major contributor to the regional accelerated melting seen in recent years. Currently, direct measurements of light absorbing aerosols (LAA), specifically BC, are very scarce in high latitudes. Three surface sites were selected for collecting snow surface samples and mobile albedo measurements. Our focus is to investigate how much of the observed change in snowmelt in southeast Iceland can be attributed to the deposition of LAA, such as BC, using the Snow, Ice, and Aerosol Radiative (SNICAR) model. Ice nucleation activity and rBC mass concentration results, using the Vienna Optical Droplet Crystallization Analyzer (VODCA) and the Single Particle Soot Photometer (SP2) respectively, will be discussed.

P2-16 Aerosol composition and origin in high Arctic

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Aerosol particles are one of the major climate forcers in the Arctic. Aerosols reflect and absorb the incoming solar radiation, modify the properties of clouds, and affect the surface albedo (Asmi et al., 2015). It is suggested that a large fraction of the increase in the surface temperature of Arctic regions can be attributed to aerosols and especially to some specific components such as sulfate and BC (Black Carbon) (Shindell et al., 2009). The chemical characterization of aerosol samples collected in the Arctic region and the identification of the spatial origin of the species is very important and will assist researchers towards understanding the factors that affect the aerosol concentrations in those regions. To address the aforementioned topics, an 18-month campaign was conducted during the period of April 2015 to December 2016 in the Research station "Ice Base Cape Baranova" (79°16.82'N, 101°37.05'E), which is located in the very northern part of the Bolshevik island to the north from Taimyr. In total 120 PM samples were collected and batches of them were analyzed using different analytical techniques. The elemental composition and concentrations of EC and OC were determined in the samples. For the elemental analysis of PM samples, the high energy, polarization geometry energy dispersive XRF spectrometer Epsilon 5 by PANalytical was used. In total the concentration of 14 elements was quantified, namely Na, Mg, Al, S, Cl, K, Ca, Ti, Mn, Fe, Cu, Zn, Ba and Pb. The elements that displayed the higher concentrations were Na and Cl which is a strong indication of the high contribution of sea spray to Arctic aerosol concentrations. For the determination of elemental (EC) and organic carbon (OC), the filters were analyzed by the thermo-optical method (Lab OC-EC Aerosol Analyzer, Sunset Laboratory, Inc.) (Diapouli et al., 2017). The concentrations of EC and OC were found to be comparable with other studies that have been conducted in the Arctic (Popovicheva et al., 2019). To identify the spatial origin of the various aerosol components, air mass back-trajectories arriving at the site have been analyzed by statistical methods. Cluster analysis was used to group trajectories into clusters depending on their direction and speed. Then, following the methodology described at Salvador et al. (2008), the incidence of different air mass transport patterns on particle concentrations and composition recorded at this station was evaluated.

P2-17 Pre-industrial to industrial changes of fossil and non-fossil contributions to dissolved organic carbon from an Alpine ice core

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Alpine ice cores allow access to continuous records of atmospheric composition back to the preindustrial era in the regions where the majority of humans live. Even though organic aerosols may have a significant effect on cloud formation and climate, to our knowledge no data has been published on long-term changes in the organic aerosol fraction. Here, we present a record of the dissolved organic carbon (DOC) concentration from Fiescherhorn ice core (Swiss Alps) over the period of 1680-1990. Correcting DOC for organic gases, taken up during snowfall, we retrieved the water-soluble organic carbon (WSOC), representing the major fraction of organic aerosols. Radiocarbon based source apportionment shows that WSOC was of non-fossil (WSOCnf) origin before 1850, with concentrations of about 75 ± 18 ppb. Anthropogenic fossil fuel input to WSOC (WSOCf) has increased since 1850 and reached non-fossil levels in the period 1960-1975. In contrast to WSOCf, WSOCnf decreased from 97 ppb in the 1870s to 44 ppb in the 1940s, after which it raised again to pre-industrial levels around 1970 and continued to increase until 1990. Our record suggests that fossil fuel emissions have significantly modified the organic aerosol since the 1850s, despite the fact that the non-fossil fraction dominated over the whole period. The overall increase of WSOCnf after 1940 is most likely related to enhanced biogenic emissions driven by the temperature increase, while the decrease after 1890 is so far unexplained.

P2-18 Long Term Trends of Black and Brown Carbon concentrations in the urban aerosol of Vienna

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The main sources for black carbon (BC) in the European urban aerosol are combustion by diesel vehicles and residential combustion, while brown carbon (BrC) originates mainly from biomass burning. In the past decades, BC concentrations have decreased in several European cities (Kutzner et al., 2018). These changes have been attributed to policies aimed at decreasing PM emissions. In our study, we investigate seasonal and long-term changes in BC and BrC for the urban aerosol of Vienna, Austria.

From January 2001 to December 2002 and from February 2014 to October 2016 urban background aerosol has been sampled and collected on quartz fiber filters. The filters were analyzed for BC and BrC content using the integrated sphere method (Hitzenberger at al., 1996, Wonaschütz et al., 2009).

Results show strong seasonal variations in BC and BrC concentrations. We demonstrate that higher BC and BrC concentrations directly correspond to cold season heating periods. BrC shows stronger seasonal variability than BC. The ratio of BrC to BC increases in winter, suggesting that biomass burning has a significant impact on wintertime particulate matter in Vienna. Furthermore, we show that BC concentrations have decreased compared to those measured in 2001 and 2002.

Hitzenberger, R., Dusek, U. and A. Berner, Black carbon measurements using an integrating sphere technique. J. Geophys. Res. (1996), 101:19601 – 19606.

Kutzner, R. D., E. von Schneidemesser, F. Kuik, J. Quedenau, E.C. Weatherhead, and J. Schmale, Long-term monitoring of black carbon across Germany, *Atmospheric Environment (2018)*, *185*, 41-52.

Wonaschütz, A., R. Hitzenberger, H. Bauer, P. Pouresmaeil, B. Klatzer, A. Caseiro and H. Puxbaum, Application of the Integrating Sphere Method to Separate the Contributions of Brown and Black Carbon in Atmospheric Aerosols, *Environ Sci Technol* 43 (2009), 1141–1146

P2-19 Comparison and trends of measured elemental carbon mass concentrations and estimated mass concentrations of black carbon in PM2.5 particle fraction

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Black smoke (BS) is a product of incomplete combustion and a pollutant generally present in inhabited zones. It is commonly known as a collection of fine solid and/or liquid particles from several nanometres to several microns. Since the usual sample mass is too small for reliable gravimetrical analysis, optical methods are commonly used for determining its mass concentration. It is of extreme importance that the mass concentration of BS not be confused with that of suspended particles. BS concentrations are determined in order to evaluate the impact on human health, because its composition may cause negative health effects, including carcinogenic ones.

The term total carbon (TC) refers to all forms of carbon present in samples of particulate matter in air; organic (OC), elemental (EC) and carbonate carbon (CC), which derive from fossil fuel combustion, biomass burning, residential space heating coal, biogenic emissions and secondary sources. EC has a long lifetime in the atmosphere and it is a visible component of particulate matter in ambient air. Particulate EC is also defined by collection and analysis. In atmospheric conditions, EC is inert, non-volatile, insoluble in solvents, and absorbs wavelengths from the visible, near infrared and ultraviolet region. It has a large specific surface area and can be a carrier of polluting gases and particles adhered to its surface transporting them deeper into the human respiratory tract.

Daily PM2.5 samples were collected continuously during a five-year period, from the beginning of 2014 to the end of 2018. The sampling station was situated in the northern residential part of Zagreb. PM mass concentrations were determined gravimetrically following EN 12341:2014. Samples were analysed for OC and EC using the thermal/optical transmittance method (TOT) with a Quartz protocol. Mass concentrations of BC, instead by aethelometry, were estimated using light absorption coefficient from BS measurements determined by a Smokestain reflectometer EEL43M.

This approach allows the estimation of the mass concentration of EC in airborne particles at multiple points without additional expensive and time-consuming analyses. It is necessary to emphasize that the model estimates the distribution parameters of a larger set of data better than individual data. The EC measured and estimated BC mass concentrations in airborne particles were well matched in the PM2.5 fraction of particles collected over the investigated period. The range of the estimated BC mass concentrations was narrower than the range of measured EC concentrations as a result of the absorption coefficient saturation in the range of high concentrations. During the measured period, the results showed a slightly decreasing trend for BC concentrations while no trend was found for EC concentrations. Both BC and EC mass concentrations showed a well-expressed seasonal dependence.

Keywords: BC, BS, BSI, EC and PM2.5

P2-20 Elemental and Organic Carbon in PM2.5 at a Coastal Urban Background Station in Croatia

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Mass concentrations of elemental (EC) and organic carbon (OC) in particulate matters with an equivalent aerodynamic diameter less than 2.5 μ m (PM2.5) were investigated in 2017 and 2018 during cold (January to March) and warm (July to September) periods of the year.

Sampling was conducted at a coastal urban background station located in Rijeka, Croatia. PM2.5 samples were collected during 24-hour periods from approximately 55 m3 of ambient air on quartz fibre filters (Pall, 47 mm) pre-fired at 900°C for 3 hours. Mass concentrations of PM2.5 were determined gravimetrically according to the standard EN 12341:2014. Carbon content was measured by the thermal-optical transmittance method (TOT) using a carbon analyser with a flame ionization detector operating according to a NIOSH-like temperature program.

In 2018, there were slight differences in the average mass concentrations of PM2.5 between the cold and warm periods, which was unexpected compared to previous measurements, while in 2017 the average mass concentrations of PM2.5 were statistically higher during the cold period. The average mass concentrations of OC and EC were higher in the cold than during the warm period. The average OC/EC mass ratio values of around 7, observed at a coastal urban background station in Rijeka, point to the influence of secondary organic aerosols.

P2-21 Sources of aerosols in the Eastern Mediterranean determined with the FLEXPART model during the A-LIFE field campaign 2017

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In April 2017, the extensive field campaign A-LIFE (Absorbing aerosol layers in a changing climate: aging, LIFEtime and dynamics, <u>https://www.a-life.at/</u>) were conducted in the Eastern Mediterranean region. Measuremnets of in-situ and lidar measurements at ground based stations and on flights with the research aircraft Falcon of the "Deutsches Zentrum fuer Luft- und Raumfahrt" (DLR) were performed. A-LIFE aims to investigate the characteristics of black carbon aerosols and their interaction with mineral dust.

For the flight paths and in-situ measurements the mass and source regions of different types of aerosol particles (dust, black carbon, sulphate) were determined by using the Lagrangian transport and dispersion model FLEXPART ("FLEXible PARTicle dispersion model"), meteorological data from the European Centre for Medium-RangeWeather Forecasts (ECMWF) and emission data from the Copernicus Atmosphere Monitoring Service (CAMS).

Methods and results of these investigations are presented and compared to observations. The Nile Delta turned out to be a dominant source region for black carbon particles. Modelled dust concentrations mostly matches the observations very well and could be assigned to different source regions such as the Arabian Peninsula and Northern Africa. Nevertheless there are also deviations such as for the 26th of April where calculated concentrations were much less as was observed in an advected dust layer of the Arabian Peninsula.

Acknowledgement: A-LIFE is funded by the ERC project 640458. We would like to thank ZAMG for providing access to ECMWF/CAMS data and the Copernicus team for their support. We also thank the whole A-LIFE team.

P2-22 The A-LIFE field experiment in the Eastern Mediterranean: studying mixtures of absorbing aerosols

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The goal of the ERC-funded A-LIFE aircraft field experiment (<u>www.a-life.at</u>) is to investigate the properties of absorbing aerosols (mineral dust – black carbon mixtures) during their atmospheric lifetime to gather a new data set on key parameters of absorbing aerosol mixtures and to study potential links between the presence of absorbing particles, aerosol layer lifetime and particle removal.

In April 2017, the DLR research aircraft Falcon was based in Cyprus and carried out measurements of the entire atmospheric column (0-12 km). The Falcon was equipped with an extensive in-situ aerosol payload, a wind lidar and meteorological sensors. In 22 research flights several outbreaks of Saharan, Arabian and Middle East dust, as well as pollution, biomass burning, and dust-impacted clouds were studied. Coordinated observations including overflights of the ground-based sites in Cyprus (Limassol, Paphos, Agia Marina), Crete (Finokalia), and Austria (Vienna, Sonnblick Observatory) were performed. The A-LIFE campaign was carried out in close coordination with the 18-month field observations conducted in the framework of CyCARE (October 2016 – March 2018) organized by the Leibniz Institute for Tropospheric Research, and with the PreTECT initiative of the National Observatory of Athens.

Highlights of A-LIFE include a sequence of six flights between 19 and 22 April 2017 which studied a Saharan dust outbreak and dust-impacted clouds while the dust outbreak moved eastwards across the Mediterranean. Furthermore, four flights between 26 and 29 April 2017 investigated Arabian/Middle East dust at altitudes below 4 km and Saharan dust aloft. In most cases, strong vertical layering of different aerosol types was observed, and the dust frequently extended up to 9-11 km. Fine mode scattering properties in the dust mixtures did not show the typical dust signature, wavelength-dependency but rather showed а of the scattering coefficient. We will give an overview of A-LIFE and available data sets, compare the properties of Saharan and Arabian dust layers, and discuss the question which aerosol component (natural vs. anthropogenic) dominates the properties in mixed aerosols. We will compare the A-LIFE observations with results from other field experiments (SAMUM, SALTRACE, ATom) over Africa, Cape Verde and in the Caribbean.

Acknowledgements: This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme under grant agreement No. 640458 (A-LIFE). Two EUFAR projects clustered with A-LIFE provided funding for 16 additional flight hours. We would also like to thank the University of Vienna, LMU and DLR for a significant amount of funding for instrumentation, aircraft certification costs, extra flight hours and aircraft allocation days.

P2-23 Long-term Measurements of Carbonaceous Aerosols in the Caribbean Region

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Carbonaceous aerosols (organic carbon (OC) and elemental carbon (EC)) contribute to regional climate change due to their ability to influence the Earth's radiative balance. Compared to many other regions, little is known about the concentrations, sources, cloud altering properties, and radiative forcing of carbonaceous aerosols in tropical coastal regions. Here we report on carbonaceous aerosols in the Caribbean island of Puerto Rico during an eight-year period from 2003-2012. Concentrations of OC and EC were determined by thermal-optical analysis of aerosols collected with pairs of quartz filters. Five-day air mass back trajectories calculated with the HYSPLIT model along with daily satellite images of aerosol optical thickness were used to understand the origin of air masses arriving at the sampling site located at a remote coastal region. HYSPLIT back-trajectories suggest that samples had the influence of air masses from North America, the Atlantic Ocean, and/or the Saharan desert. Analysis of backup filters indicated that 50% of the OC collected on front filters was gas-phase rather than particulate-phase OC. Thus, if the correction of the positive artifact is not performed, OC concentrations will be significantly overestimated at this location. Particle organic matter (POM) was determined from OC concentrations assuming a conversion factor of 1.8. POM concentrations varied with season, with lower concentrations in the summer (average 94 ng/m3) than in the winter (average 248 ng/m3). Samples collected during African dust events showed lower mass concentrations of TC (average 130 ng/m3) than days with absence of African dust (270 average ng/m3). These results show that concentration of carbonaceous fractions aerosols are influenced by seasonal variations and African Dust incursions. Detailed results for the eight-year period will be presented at the conference.

P2-24 One-year semi-continuous hourly measurement of carbonaceous aerosol in the Beijing-Tianjin-Hebei region of China: concentration levels, spatial and temporal variation, and source identification

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A one-year hourly measurement (from December 1, 2016 to November 30, 2017) of organic carbon (OC) and elemental carbon (EC) in fine particulate matter was performed using semi-continuous OC/EC analyzers in Beijing, Tianjin, Shijiazhuang and Tangshan in the Beijing-Tianjin-Hebei (BTH) region in northern China. The annual average concentrations (± associated standard deviation) of OC and EC were 11.0±10.7 and 3.4±3.3, 12.0±9.8 and 3.1±3.6, 22.8±30.6 and 5.4±6.5, and 12.1±9.6 and 3.5±3.6 µg/m3 for Beijing, Tianjin, Shijiazhuang and Tangshan, respectively. The carbonaceous aerosol levels (the sum of the OC multiplied by 1.4 and the EC concentration) accounted for 32 %, 29 %, 37 % and 28 % of the PM2.5 mass values in the four sites, indicating that the carbonaceous fraction provides a substantial contribution to the fine particle mass. There was a strong seasonality in the OC and EC concentrations with higher levels in autumn and winter and lower ones in spring and summer. A pronounced double-peak diurnal pattern occurred for OC in all four seasons at all four cities, with one peak occurring between approximately 6:00 and 10:00, which could have resulted from the combination of vehicular emissions in the morning and secondary OC (SOC) formation caused by incremental solar radiation, and the other peak occurring during the evening traffic rush hour, which even lasted until the next early morning. Also EC and the OC/PM2.5 and EC/PM2.5 ratios exhibited the pronounced double-peak diurnal pattern, indicating that there was a substantial impact from traffic emissions. Our OC and EC levels were lower than published data from the past two decades for the BTH region, implying some effect of recent measures for improving the air quality. The regression lines of OC versus EC were examined for each of the four seasons and over the full year for the four sites. Significant correlations (p < 0.001) were found throughout the study period with high slopes and correlation coefficients in winter, but low slopes and correlation coefficients in summer. The estimated SOC based on the minimum R squared (MRS) method accounted for 14.7-47 %, 21-74 %, 21-55 % and 17.0-74 % of the OC for Beijing, Tianjin, Shijiazhuang and Tangshan, respectively, with annual percentage SOC/OC ratios of 29 %, 47 %, 38 % and 48 %. There was a tendency for our ratios to be larger than previous ratios obtained for the BTH region in the past decade, which is mainly attributable to the difference in estimating SOC. There were obvious differences in the potential source regions of OC and EC among the four cities. Obvious prominent potential source areas of OC and EC were observed for Beijing, which were mainly located in the central and western areas of Inner Mongolia and even extended to the Mongolian regions, which is different from the findings in previous studies. For all sites, adjacent areas of the main provinces in northern China were also found to be important potential source areas.

P2-25 Monitoring and analysis of aerosol optical properties over an urban city in India

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In order to understand the impact of atmospheric aerosols on climate, it is essential to know their optical properties as well as spatial and temporal variability. The present study is focused on the megacity Delhi which is one of the most polluted urban regions in the world. Aerosol Optical Depth (AOD) is an important aerosol optical property which has been spatially and temporally analyzed over the urban city of Delhi and surrounding areas in North India, using the satellite and ground based instrument measurements. The satellite remote sensing of aerosol is advantageous due to its extensive and continuous spatial coverage and lower cost for acquisition. In this study, the relationship between land-use structure and satellite retrieved AOD has been analyzed for the first time over Delhi and the impacts of topography on the aerosol distribution has been discussed. It is observed that there is a clear correlation between the aerosol characteristics and land use pattern of the mega city. Also, the satellite data is statistically verified and validated with the ground based sky radiometer instrument installed at Indian Meteorological Department, New Delhi. The AOD product is retrieved from two satellites, MODIS and INSAT-3D for validation with the ground based multi-wavelength Prede Sun/sky radiometer (POM-02). Higher correlation coefficient is found in case of MODIS than INSAT-3D. Further the impact of a severe dust storm on the aerosol optical properties and radiative forcing over Delhi is presented in the study. In this section of the study, the data is measured using ground based skyradiometer instrument and Skyrad.Pack software to analyse the aerosol optical properties over Delhi during an unusual dust storm that occured on 31st May 2014. The aerosol characteristics were further utilized to calculate radiative forcing using SBDART (Santa Barbara DISORT Atmospheric Radiative Transfer) model.

P2-26 Reactive Oxygen Species Formed by Air Particulate Matter in Aqueous Phase

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Reactive oxygen species (ROS) play a central role in adverse health effects of air pollutants (Pöschl and Shiraiwa 2015). Respiratory deposition of fine particulate matter (PM2.5) can lead to the formation of ROS in epithelial lining fluid, potentially causing oxidative stress and inflammation (Shiraiwa et al., 2017). Secondary organic aerosols (SOA) account for a large fraction of PM2.5 (Hallquist et al., 2009), but their role in adverse health effects of PM2.5 is unclear (Tong et al., 2018). We quantify and compare the ROS yields of laboratory-generated SOA and ambient PM2.5 in pure water. The laboratory-generated SOA from biogenic (α -pinene, β -pinene, limonene, and isoprene) and anthropogenic (naphthalene) precursors were found to produce 0-12% ROS (radicals and H2O2, molar yield) in water. The ROS yields of these SOA showed a positive correlation with the abundance of organic peroxides in them. Our findings suggest that SOA may play an important role in the ROS formation and adverse health effect of air particulate matter.

Hallquist et al., *Atmos. Chem. Phys.*, 9, 5155-5236, 2009.
Shiraiwa, M. et al., *Environ. Sci. Technol.*, 51, 13545-13567, 2017.
Pöschl, U., and Shiraiwa, M. *Chem. Rev.*, 115, 4440-4475, 2015.
Tong et al., *Environ. Sci. Technol.*, 52, 11642-11651, 2018.

P2-27 Reduction potential as an indicator for ROS formation of organic aerosols

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Exposure to fine particulate matter with size of $\leq 2.5 \ \mu m$ (PM2.5) may cause respiratory inflammation and diseases upon generating excessive reactive oxygen species (ROS) after inhalation in the human lung (Pöschl and Shiraiwa 2015). There are several methods to determine the oxidative potential measuring different end-points (measuring depletion of dithiothritol, antioxidants or quantifying the yield of certain ROS) which can lead to different results (Calas et al., 2018). As one of the most important ROS, H2O2 can be generated upon interactions of redox active PM2.5 components with water and antioxidants (Lakey et al., 2016). Due to a lack of understanding of the organic aerosol (OA) composition (Noziére et al. 2015) and complex interactions between different constituents of the particles (Charrier et al., 2014; Wang et al., 2018), the formation mechanism and yield of ROS by OA in physiological conditions are largely unknown. Therefore, we measured the H2O2 yields of a selection of atmospherically relevant oxygenated and nitro-polycyclic aromatic compounds (e.g., quinones) in a surrogate lung fluid as well as the dithiothreitol (DTT) depletion behavior in a respective assay. We found that both parameters for the investigated compounds had a good correlation with their reduction potential, which describes the tendency of a molecule to acquire electrons (de Heer, 1950). Based on this correlation, we suggest that a database of reduction potentials can be used to estimate the H2O2 yield of different redox active components in OA. Finally, the reduction potential may become a useful indicator to describe the capacity to form other types of ROS, beyond H2O2 and thereby deplete antioxidants.

Pöschl, U., and Shiraiwa, M. Chem. Rev., 115, 4440-4475, 2015.

Calas, A., Atm. Chem. Phys., 18, 7863-7875, 2018.

Lakey et al., Sci Rep, 6, 32916, 2016.

Noziére et al., Chem. Rev., 115, 3919-3983, 2015.

Charrier et al., Environ. Sci. Technol., 48, 7010-7017, 2014.

Wang et al., Atmos. Chem. Phys., 18, 3987-4003, 2018

de Heer, J.: Quantum Mechanical Study of the Oxidation-reduction Potentials of Quinones, D. B. Centen, 1950

Posters 3

2.5 Carbonaceous CCN and INPs

P3-1 Black carbon impact on atmosphere of World Heritage lake Baikal

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Lake Baikal, situated in south-east Siberia, is the deepest (1700 m) and oldest (25 million years) lake in the world. It contains 20% of world's total freshwater reserve. Known as the "Galapagos of Russia", its unusual freshwater faunas and ecosystem have produced an exceptional value for environmental science, being assigned to UNESCO World Heritage site.

Numerous emissions from industrial and residential sources as well as increased forest fires have led to recent harmful cyanobacterial blooms in the near-shore waters, rise of chlorophylla and decrease of water transparency, which are indicators of eutrophication of Lake Baikal due to anthropogenic effects. In summer 2018, in a season of Siberian wildfires, the ship - based expedition exploring the Baikal atmospheric aerosol loading and ecosystem was performed over the lake area. It was supported by three simultaneously operated ground stations to increase data gathered to take atmosphere pollution research to the next level. Active and passive sounding (lidars and photometers) as well as nephelometers, aerosol counters, high volume samplers, and impactors were used. For the first time the distribution of black carbon (BC) concentration over Baikal water area was obtained by mobile portable aethalometer. Such approach allows to evaluate interrelations between changes of the spatial structure of aerosol loading, spectral light absorption, size distribution, and the chemical composition with a meteorological and synoptic situation.

The BC spatial-temporal variability is non-uniform over the lake water area. Extended areas with low background (less $0.4 \ \mu g/m3$) are defined in the north, in remote areas from residential sources, and in reserved regions. Air transport from south coastal territories increases BC up to $2 \ \mu g/m3$, indicating the impact of large harbors, cities, industrial areas of Irkutsk and gas flaring fields. Elevated values of absorption angstrom exponent (AAE) up to 3.5 emphasis the coal burning on thermal plants and residential biomass burning. The impact of shipping emissions, up to $5 \ \mu g/m3$ is purposely observed for the touristic and resort places. Orographic features of a Baikal coastal zone such as gulfs, bays, large river beds, and the hills in which temperature inversions are more often formed, are found having the particular impact on BC. They accumulate the pollution at high concentrations, as found near one of the largest gulfs of Baikal, the Barguzin gulf. Significant increase of BC up to $2 \ \mu g/m3$ relating with AAE around 2 is observed during the smoke event, covered the lake water area along the east coast. At this time on-ship, satellite and ground station lidar observations of high - altitude stratification show the high aerosol concentrations in the lower troposphere (0.1-4 km) of Central Baikal, caused by smoke transported from the intensive wildfires in the Yakutia and Krasnoyarsk kray.

Work is supported by RFBR-OFI № 17-29-05044 and RFBR № 18-29-05044

P3-2 A new analytical approach for estimating hygroscopic properties of soot aerosols by considering their size distribution and morphologies

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Soot particles are considered as important aerosols in the atmosphere due to their potential role as cloud condensation nuclei (CCNs). Freshly released soot is generally considered as hydrophobic. However, the so-called aging process in the atmosphere can modify size, morphology and surface composition of soot particles and turn them into efficient CCNs. The hygroscopic properties of soot are commonly measured from their activated fraction Fa that is the ratio of the number of nucleated droplets on the number of CCNs. For spherical and monodisperse aerosols, the κ -Köhler theory is often used to obtain the parameter κ in an attempt to quantify the hygroscopic properties of aerosols. In this work, a model to obtain κ is proposed that takes into account the size distribution and the morphology of the soot particles. The model is initially tested on dry ammonium sulfate that is well known to produce quasi-spherical particles: the results of the activation experiments are in good agreement with the predictions of the model. Then, the model is applied to soot particles that are characterized by complex morphology. Soot particles had to be activated by aging with ozone to increase their κ into the validity range of the model (i.e. to turn fresh soot to hydrophilic aggregates). The parameters of the determination of κ are soot particle mobility diameter dm, fractal dimension Df, the primary particle diameter dpp and the geometric standard deviation of volume equivalent particles of soot.

P3-3 Impact of the exposure of kerosene soot to O3 and SO2 on its hygroscopic properties

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Soot particles are generally considered as poor ice nuclei (INs) or cloud condensation nuclei (CCNs). After the emission from the aircraft jet engines, the so-called aging process in the atmosphere can induce morphology and chemical modifications at the particle surface that change the soot hygroscopicity. For a better understanding of the atmospheric aging, the interaction of soot particles with O3 and SO2 is investigated that are well-known oxidant and pollutants in the atmosphere.

In this work, soot particles are generated from a laboratory diffusion flame supplied with kerosene to reproduce some critical properties of aviation soot like the particle size distribution and surface composition. The soot particles are injected in the atmospheric simulation chamber CESAM where they are mixed with O3 and SO2 in controlled conditions of temperature, pressure and relative humidity. The activation of soot particle is measured experimentally by a cloud condensation nuclei counter (CCNc) and a condensation particle counter (CPC) in parallel. The morphology of fresh and aged soot is assessed by transmission electron microscopy (TEM). In order to quantify the hygroscopic property of the soot particle, a modified version of the κ -Köhler theory that considers the particle size distribution and morphology is proposed.

P3-4 The impact of isolated atmospheric ageing processes on the CCN activity, density, and fractal dimension of soot particles

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Soot particles (SPs) are a special type of atmospheric particles as determination of their physical and chemical properties is challenging due to their fractal structure and their refractive nature. While they are hydrophobic at the time of emission, nevertheless they are found in hydrometeor residuals. This could be due to incorporation into existing hydrometeors (e.g. impaction scavenging). The option of atmospheric ageing causing SPs to become cloud condensation nuclei (CCN) is still debated within the atmospheric science community.

We present results of the impact of isolated ageing processes on the density and fractal dimension of SPs and relate these to changes in CCN activity determined in parallel. The experiments have been performed within a 3m3 stainless steel tank run in continuous flow stirred tank reactor (CSTR) mode. This experimental design allowed to execute the experiments at atmospherically relevant conditions (e.g. 20 to 200 ppb O3 concentration). Further, aging durations of up to 16 h were achieved resulting in a high comparability to ambient conditions.

SPs of two types were produced by a miniCAST soot generator. One was rich in organic carbon content (CBW) while the other one exhibited a significantly lower organic carbon content (CBK). Size-selected particles were aged by heterogeneous O3 oxidation, coated in situ with alpha-pinene ozonolysis products (i.e. secondary organic aerosol; SOA), or with sulfuric acid (H2SO4). The mobility diameter, the single particle mass, and the CCN activity of the particles was recorded prior as well as after each individual ageing process.

While neither of the non-aged soot types showed any CCN activity, the activity progressively increased upon O3-oxidation, SOA coating, and H2SO4 coating (conducted in separate experiments). Utilizing the activation time analysis concept, which is a mathematical framework allowing for the analysis of non-gradual transitions such as CCN-activity from CSTR data, we determine the minimal ageing time (*t*act) for activation to be 1h:50min at a super saturation (SS) of 1.4% and 8h:30min at 0.6% SS for CBW upon O3 oxidation at 200 ppb. The ageing time had to be extended 5 to 6-fold to cause similar CCN activity of CBK at the same conditions. Coating with alpha-pinene SOA reduced *t*act to 35min at 1.4% SS and 3h:45min at 0.6% SS for both soot types. Coating with H2SO4 (6 to 30% of initial particle mass) caused immediate activation of the entire particle population.

Investigation of the fractal dimension shows that no significant difference between the non-aged particles (CBW = 2.05, CBK = 2.25) can be determined upon O3-oxidation or H2SO4 coating. Opposite to this, the fractal dimension increases to 2.25 and 2.43 for CBW and CBR, respectively, upon SOA coating. The same evolution in density also corroborates this finding. These results show, that atmospheric ageing processes can lead to a significant change in CCN activity without impacting the fractal nature of SPs.

P3-5 CCN-activation of soot particles after exposure to ambient Ozone concentrations. A discussion of the impact of the residence time distribution in continuous flow aerosol chambers.

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Freshly emitted soot particles are known to be poor cloud condensation nuclei (CCN), but atmospheric measurements indicate that some soot particles act as CCNs. Soot particles have an average atmospheric lifetime of one week during which they are exposed to different aging processes. One process, which might cause CCN activity, is the heterogeneous oxidation of these particles. The investigation of such processes in the laboratory is an experimentally challenging task due to the long time span, which has to be covered to achieve comparability to atmospheric aging. Generally, two experimental approached are used for that.

1. Soot particles are treated with high oxidant concentrations (up to 1000 x atmospheric average). This approach reduces the observation time needed but does not consider potential non-linear reaction kinetics or partitioning.

2. Larger aerosol chambers can used that extend the observation time by extending the chamber volume. Besides potential financial restrictions this approach has further limitations since running experiments with e.g. initially size selected aerosol particles is very challenging.

We adapted the Continuous Flow Stirred Tank Reactor (CSTR) concept to achieve long observation times (<16 h) in a rather small chamber (3 m3). This allows running experiments at ambient conditions as well as with low aerosol concentrations of <500 /cm3. We present the mathematical framework, which we developed to retrieve information on non-gradual transitions, e.g. CCN activation from such CSTR-experiments. Usage of the new metric activation time (tact) expands the potential of data analysis beyond the calculation of means. The concept was verified on various data sets, including the investigation of the change in CCN-activity of soot particles due to heterogeneous O3 oxidation, e.g. 100 nm size selected particles exposed to a constant ozone concentration of 200 ppb. At an atmospherically relevant supersaturation (SS) of 0.4 % we determine an activation time of 8h for a CAST soot sample rich in organic. Even an increase to 1.0 % SS still results in a tact of 4h. CAST samples low in organics were found to need a 5 to 6 times longer aging time in order to reach the same level of CCN-activity. These results highlight the need for long-time laboratory experiments for the investigation of such atmospheric processes. We show further that tact can be applied to any non-gradual transition data originating from other oxidation flow reactors such as the PAM chamber widely used in atmospheric science. By incorporating the chamber specific residence time distribution, our concept is even capable of explaining discrepancies in experimental results originating from different chambers as seen in intercomparison studies. Therefore, application of our analysis concept will allow for further insights to atmospheric aging processes in future experiments as well as by reanalysis of already existing data.

P3-6 Molecular insight on organic matter's ice nucleating ability in immersion freezing

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Organic aerosols represent a subset of atmospheric particles able to act as cloud condensation nuclei (CCN) and, as more recently found, ice nucleating particles (INPs). CCN and INPs affect the ratio of water and ice in mixed-phase clouds, leading to an impact on Earth's radiative balance. In this work, we use dissolved organic matter (DOM) as a proxy for organic aerosols and lake spray aerosols in ice nucleation experiments. As the dominant IN mechanism in mixed-phase clouds is immersion freezing, we investigated the ability of DOM to act as INPs, using our homebuilt DRop freezing Ice Nucleation Counter Zurich (DRINCZ). We use field collected DOM and purchased DOM standards from the International Humic Substance Society and find that DOM, despite coming from different locations, shows consistent ice nucleating abilities above our instrument's detection limit of -22.5 °C with a spread we attempt to parameterize using organic carbon properties. Furthermore, DOM is a complex mixture of organic matter, proteinaceous material, humic-like substances, lignin, organic acids and some ions. To address this complexity and to determine the ice-active subcomponent of DOM, we have investigated the ice nucleation ability of lignin polymeric material. We find that lignin is also ice-active and that atmospheric processing such as exposure to ozone and sunlight decreases the ability of lignin to act as an ice nucleating particle. In sum, we will present a laboratory-based chemical perspective on the ability of organic material present in the atmosphere to nucleate ice.

P3-7 Lysinibacillus parviboronicapiens, a precipitation-associated Gram-positive bacterium that secretes submicron sized nonproteinaceous ice nuclei

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Two bacterial isolates with ice nucleation activity (INA) were previously isolated from a freezing rain sample and identified as members of the genus *Lysinibacillus* based on 16S rRNA sequencing. The isolates were found to secrete submicron sized, heat-resistant, and proteinase-resistant ice nuclei. A comparative genomics approach revealed that the two isolates belong to the *Lysinibacillus parviboronicapiens* species. Testing the majority of *Lysinibacillus* species for INA further suggested that *L. parviboronicapiens* is the only *Lysinibacillus* species with INA. To determine the genetic and chemical basis of INA in *L. parviboronicapiens* the genome sequences of the *L. parviboronicapiens* strains with INA have been compared with all available genome sequences of other *Lysinibacillus* species without INA. The expression level of all *L. parviboronicapiens* genes was also determined. Finally, *L. parviboronicapiens* strains were exposed to UV radiation to obtain mutants without INA. Nine such mutants were obtained. The genomes of these mutants were also sequenced. Combining the results from all these experimental approaches, genes for a biosynthetic pathway were identified as candidate genes that may be responsible for INA in *L. parviboronicapiens*. Currently, these genes are being used in additional experiments to determine if they are necessary and sufficient for INA of *L. parviboronicapiens*.

P3-8 Coal fly ash as good ice-nucleating particles in cirrus cloud conditions

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Coal fly ash (CFA) particles are one of the by-products resulting from coal combustion. These particles, when emitted into the atmosphere, can directly or indirectly affect the solar radiation budget. Specifically, CFA particles may alter cloud microphysical properties by acting as icenucleating particles. Recent studies show that CFA particles can nucleate ice in the immersion mode but our current understanding of the behaviour of CFA particles as ice-nucleating particles at condition relevant for the cirrus clouds is highly limited. In this study, we investigated the icenucleating efficiencies of CFA particles from different sources in the Aerosol Interaction and Dynamics in the Atmosphere (AIDA) aerosol and cloud simulation chamber. All the CFA samples that we studied showed a significant ice nucleation activity at relative humidity with respect to ice (104 % - 138 %) evaluated at the maximum relative humidity with respect to ice reached during each experiment, in the temperature range from 214 K to 251 K. In order to compare their ice nucleating efficiencies, we calculated the ice nucleation active surface site densities of these particles as between 109 – 1011 m-2 within the same temperature coverage of our experiments. We conclude that CFA particles are efficient ice-nucleating particles in the cirrus cloud conditions. This means that CFA particles may potentially contribute to regional cold cloud ice nuclei budget, especially close to the source where these particles are emitted.

P3-9 The Ice Nucleation Activity of Black and Brown Soot Aged by Exposure to NO2 and SO2

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The ice nucleation activity (INA) of soot was studied experimentally. Two different types of soot were produced by burning a propane-air mixture under controlled conditions with a miniCAST (combustion aerosol standard, Jing Ltd) burner. Depending on the mixture proportions of the burner, soot with high and low organic content was obtained. Subsequent reactions of the soot with NO2 and SO2 were carried out in a reaction chamber with exposure times between 30 and 360 minutes. Untreated and treated soot samples were analyzed for their INA in immersion freezing experiments. Their composition was analyzed via X-ray photoelectron spectroscopy; their microstructure was studied via Raman spectroscopy and their morphology was analyzed via transmission electron microscopy. We showed that the INA of soot with a high composition of organic material increased significantly after a reaction with NO2 and SO2. The heterogeneous mean freezing temperature was increased by 10-12 °C to approximately -25 °C. Untreated and NO2-treated black carbon showed no INA, but after 30 minutes of SO2 exposure, the heterogeneous mean freezing temperature shifted by 15 °C to -22 °C. Analytic analyses revealed that the surface composition and the degree of graphitization impact the INA. The interplay among the properties relevant for ice nucleation such as the chemical composition and the microstructure of the soot's surface, which are closely related to each other, is important and needs to be considered when predicting the ice nucleating ability of soot.

2.6 Bioaerosols

P3-10 Extraction and size distribution measurements of subparticles released by pollen grains

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During the blooming season of plants, pollen is a persistent component of the atmospheric aerosol. Although sexual reproduction of plants is the main function of pollen, once airborne in the atmosphere, pollen grains can also impact human health (e.g. hay fever) and cloud formation (Augustin et al. 2013, Pummer et al. 2012). It is known that under certain conditions many species of pollen rupture and release smaller particles and other material from the interior of their grains, commonly referred to as sup-pollen-particles (SPP). These SPP have been shown to act as cloud condensation nuclei (Steiner et al. 2015).

In this study we developed a method to extract material from pollen grains by rupture due to mechanical stress. We apply this method to five different pollen species (*Betula pendula, Phleum pretense, Poa pratensis, Corylus avellana, Artemisia vulgaris*) and find that pollen grains of *Betula, Phleum, Poa* and *Corylus* contain both, soluble and particulate material, whereas those of *Artemisia* only contain soluble material. We further separate the SPP from the soluble material and investigate their size distribution and shape. The size distribution of the resuspended SPP was measured using a TSI Aerodynamical particle sizer. In addition, we examined the geometric size and shape of SPP with a Scanning Electron Microscope (Zeiss Supra 55 VP). Furthermore, an estimation of SPP mass contained in the pollen grains was done.

P3-11 Investigating sub-particles of pollen with a single particle mass spectrometer

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Pollen have gained increasing attention over the last decades due to their ability to impact cloud microphysics by acting as cloud condensation nuclei and ice nuclei. Recently, laboratory studies have shown that the cloud forming potential of pollen grains is governed by macromolecules that can be washed off from pollen grains when left in water for several hours (e.g. Pummer et al. 2015). As well, it is known that pollen can rupture under specific conditions (e.g. Taylor et al. 2004) and release material from their inside i.e. cytoplasmic material, commonly referred to as sub-particles. These sub-particles are likely to act as cloud condensation nuclei (Steiner et al. 2015). However, information on the presence and distribution of such particles in the atmosphere is scarce and a method to identify sub-particles is lacking.

In this study we develop a method to induce pollen rupture by mechanical stress. We apply this method to five different pollen species (*Betula pendula, Phleum pratense, Poa pratensis, Corylus avellana, Artemisia vulgaris*) and extract soluble and solid cell material. We find that four of the five investigated pollen species contain particulate material in the size range from a few hundred nanometer to a few micrometer. We investigate these particles with the laser ablation single particle mass spectrometer (LAAPToF) of the University of Vienna. The sub-particles are aerosolized with a nebulizer, dried and introduced into the LAAPToF. The LAAPToF uses a 193 nm Excimer laser to ionize single particles and a bipolar time-of-flight mass spectrometer to obtain positive and negative mass spectra of the ions produced by each particle. Aerodynamic particle sizing is achieved with two 405 nm scattering lasers. For each pollen species we obtain mass spectra of the sub-particles and highlight characteristic features that might help to identify such particles in the atmosphere.

References

Pummer et al. 2015. Atmos. Chem. Phys., 15, 4077–4091. Taylor et al. 2004. Clin. Exp. Allergy, 34, 1591–1596. Steiner et al. 2015. Geophys. Res. Lett., 42, 3596–3602.

P3-12 Contribution of Bioaerosols to the Ice Nucleation Activity of Aerosol Particles in the Boreal Forest

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Cloud processes in the Earth's atmosphere are strongly affected by ice-nucleating particles (INPs), which trigger the formation of ice crystals in clouds and thereby markedly influence the initiation of precipitation, the life cycle of clouds and their radiative properties. The ice nucleation activity in low latitudes is dominated by mineral dust particles, which are generally highly ice active (DeMott et al., 2003). The abundance and sources of INPs in higher latitudes, especially in boreal forest regions, where mainly biogenic aerosol particle types are prevalent, has not yet been investigated in a systematic approach.

The field campaign HyICE2018 was originated by the University of Helsinki and the Karlsruhe Institute of Technology (KIT), aiming at performing comprehensive long-term INP measurements in the Finnish forest. The campaign took place in Hyytiälä in Southern Finland at the University of Helsinki SMEARII research station (Hari and Kulmala, 2005) from February to June 2018.

During the HyICE2018 campaign, KIT provided the INSEKT (Ice Nucleation Spectrometer of the Karlsruhe Institute of Technology) to analyse the INP content of ambient aerosols sampled on filters. INSEKT is able to measure INP concentrations in suspensions at temperatures between 273 K and 248 K. In addition, the University Tampere provided a WIBS instrument for the detection and characterization of fluorescent biological aerosol particles.

In the long-term time series of measured INP concentrations, a systematic seasonal trend is observed in the temperature range between 255 K and 259 K. Here, the concentration increased by about two orders of magnitude from winter to spring in this temperature range. The correlation to meteorological data, like ambient air temperature and snow depth is examined. WIBS-measurements are considered to confirm the role of bioaerosols to the increasing ice nucleation activity. Also, they are used to investigate the size dependence of INPs in the boreal environment, which gives additional information about the prevalent INP types. Further investigations of INP types that contribute to the ice nucleation activity in the boreal forest have been conducted via heat treatment tests of the collected aerosol samples. High heat sensitivity can indicate to INP composed of proteins or other biological materials (McCluskey et al., 2018). INP spectra measured during HyICE2018 are affected by heat treatments along the entire temperature range. In addition, the heat tests indicate that not only the INP concentration in the boreal forest is changing in the transition period from winter- to springtime, but also the INP type.

DeMott et al. (2003), Geophys. Res. Let. 30 (14). Hari and Kulmala (2005), Boreal Environ Res. 14, 315-322. McCluskey et al. (2018), J. Geophys. Res.: Atmospheres 123 (11), 6196-6212.

P3-13 Species Richness, rRNA Gene Abundance, and Seasonal Dynamics of Airborne Plant-Pathogenic Oomycetes

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Oomycetes, also named Peronosporomycetes, are one of the most important and widespread groups of plant pathogens, leading to significant losses in the global agricultural productivity. They have been studied extensively in ground water, soil, and host plants, but their atmospheric transport vector is not well characterized. In this study, the occurrence of airborne Oomycetes was investigated by Sanger sequencing and quantitative PCR of coarse and fine particle aerosol samples collected over a 1-year period (2006–2007) and full seasonal cycle in Mainz, Germany. In coarse particulate matter, we found 55 different hypothetical species (OTUs), of which 54 were plant pathogens and 29 belonged to the genus Peronospora (downy mildews). In fine particulate matter (<3 µm), only one species of Hyaloperonospora was found in one sample. Principal coordinate analysis of the species composition revealed three community clusters with a dependence on ambient temperature. The abundance of Oomycetes rRNA genes was low in winter and enhanced during spring, summer, and fall, with a dominance of Phytophthora, reaching a maximum concentration of $\sim 1.6 \times 106$ rRNA genes per cubic meter of sampled air in summer. The presence and high concentration of rRNA genes in air suggests that atmospheric transport, which can lead to secondary infection, may be more important than currently estimated. This illustrates the need for more current and detailed datasets, as potential seasonal shifts due to changing meteorological conditions may influence the composition of airborne Oomycetes. An insight into the dynamics of airborne plant pathogens and their major drivers should be useful for improved forecasting and management of related plant diseases.

Lang-Yona N, Pickersgill DA, Maurus I, Teschner D, Wehking J, Thines E, Pöschl U, Després VR and Fröhlich-Nowoisky J (2018) Species Richness, rRNA Gene Abundance, and Seasonal Dynamics of Airborne Plant-Pathogenic Oomycetes. Front. Microbiol. 9:2673. doi: 10.3389/fmicb.2018.02673

2.7 Optical properties of carbonaceous aerosols, radiative forcing and climate

P3-14 Do All Black Particles Contain Black Carbon?

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Black carbon is often thought to dominate particle light absorption due to its high bulk absorption coefficient. Here, we examine some manifestations of small black particles in our everyday lives including the ubiquitous blackening of bicycle chains, climbing ropes, and motor oil. We present experimental and theoretical evidence that this blackening is caused by black metal nanoparticles, not by black carbon. While metals are commonly thought of being highly reflective, this is only true if the imaginary part of the refractive index and its product with the size parameter x are both larger than \sim 3 (Sorensen et al., 2019); this is generally true for metals in our everyday experience. However, for metallic nanoparticles, the second condition is generally not fulfilled and metal particles become black and highly absorbing with a very low single scattering albedo (Moosmüller and Sorensen, 2018) and with an appearance resembling that of black carbon.

References:

Sorensen, C. M., J. B. Maughan, and H. Moosmüller (2019). Spherical Particle Absorption over a Broad Range of Imaginary Refractive Index. *J. Quant. Spectrosc. Radiat. Transfer*, accepted for publication.

Moosmüller, H. and C. M. Sorensen (2018). Small and Large Particle Limits of Single Scattering Albedo for Homogeneous, Spherical Particles. *J. Quant. Spectrosc. Radiat. Transfer*, **204**, 250-255, https://doi.org/10.1016/j.jqsrt.2017.09.029.

P3-15 Optical Properties of Aerosol Emitted from the Open Combustion of Cheatgrass (Bromus Tectorum)

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Cheatgrass (Bromus tectorum) is a non-native, invasive annual grass species in the U.S. Intermountain West that plays an important role in fire ecology. Its ubiquitous presence has greatly increased frequency and extent of rangeland fires by creating higher fuel loads and dense vegetative coverage in areas where shrubs and desert grasses were once separated by open areas of soil. However, next to nothing is known about aerosols emitted from the open combustion of cheatgrass. Cheatgrass burns primarily in the flaming combustion phase where large amounts of black carbon aerosols are emitted. These emissions contribute to air pollution events, affect the radiative budget and climate change, and can cause severe health effects.

Laboratory open combustion of cheatgrass was performed in the biomass combustion chambers of the Desert Research Institute to measure optical properties and chemical composition of the emitted combustion aerosols. Here, we will discuss 1) optical emission factors, 2) physical aerosol properties, and 3) optical aerosol properties determined by photoacoustic and nephelometric measurements of absorption and scattering coefficients of cheatgrass combustion emissions.
P3-16 Modification of Snow Surface Reflectivity Spectra through Brown Carbon Aerosol Deposition

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Brown carbon (BrC) is a form of organic carbon emitted from combustion processes with a brownish or yellowish visual appearance, caused by enhanced light absorption at shorter visible and ultraviolet wavelengths. Recently, optical properties of BrC aerosols have become the topic of intense research, but little is known about how BrC deposition onto snow surfaces affects the snow albedo spectrum and the resulting radiative forcing.

We generated BrC through small-scale, smoldering biomass combustion and deposited it onto natural snow surfaces in the Carson Range of the Sierra Nevada, USA. After deposition, we monitored the spectral reflectivity of these disturbed snow surfaces and of adjacent undisturbed snow surfaces and observed a strong reduction of snow surface reflectivity in the blue and ultraviolet spectral regions. We also will discuss (1) the temporal evolution of the snow surface reflectivity after BrC deposition, (2) modeling results for the influence of deposited BrC on snow surface albedo, and (3) BrC-on-snow radiative forcing.

P3-17 Enhanced light absorption of aerosol particles in fresh snow samples

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Airborne particles such as black carbon, mineral dust and biological particles are emitted and transported in the the end they will be precipitated on the earth surface. Even small amounts of light absorbing particles are able to darken the snow surface, and therefore reduce the snow albedo. A reduced snow albedo might enhance snow melting processes in arctic, antarctic and glacier regions. Usually the albedo reduction due to aerosol particles is estimated on mass concentrations of refractory black carbon that are deposited in the snow. Since other aerosol components also contribute to visible light absorption this estimate of albedo reduction might turn out to be too low. To quantify the contribution of all light absorbing aerosol components in the snow we combine the determination of refractory black carbon mass concentrations and the visible light absorption coefficients of the aerosol particles in the snow. For a set of snow samples collected during the winter 2016/2017 at the Environmental Research Station Schneefernerhaus (UFS) at 2650 m a.s.l. the absorption properties were specified. Therefore the melted snow samples had been aerosolized by an efficient nebulizer. Combining the three wavelength photo acoustic absorption spectrometry with the single particle incandescence measurement (SP2) the spectral absorption coefficients and the refractory black carbon mass of the particles of the snow were determined.

Our findings show an enhanced light absorption of the aerosol released from the snow sample compared to the absorption derived from the refractory black carbon mass. Additionally asurements by Environmental Scanning Electron Microscopy (ESEM) and single particle fluorescence with the Waveband Integrated Bioaerosol Sensor (WIBS-4) revealed a significant portion of biological material within the snow samples.

P3-18 Annual Behavior of Angstrom Exponent of the Aerosol Absorption Coefficients in visible from the Measurements in 2010-2017 in West Siberia

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Last decades, the peculiarities of spatial-temporal variability of the BC concentration and the atmospheric aerosol absorption coefficients are the subject of careful study in different regions. Considerable attention is paid to the study of the dynamics of the Angstrom exponent of the aerosol absorption in the wavelength range 370-950 nm and development of methods for separating the contribution of the absorbing substance generated by various natural and anthropogenic sources of aerosol and BC emission.

In this paper we study the peculiarities of the annual behavior and the inter-annual variability of monthly average values of the Angstrom exponent on the basis of measurements in 2010-2017 in the near-ground air layer of West Siberia. Round-the-clock measurements had carried out at the Aerosol station of IAO SB RAS by means of MDA aethalometer designed at IAO SB RAS. The instrument was inter-calibrated in situ during measurements together with MAAP 5012 photometer, and records the aerosol absorption coefficients at wavelengths 460, 530 and 630 nm, which allow to estimate the average values of the Angstrom exponent a. Angstrom parameters are actively used last years for development of the techniques for estimating the contribution of black carbon and brown carbon into the aerosol matter.

It is revealed that the annual behavior of the monthly average values of a is characterized by minimum values $\sim 1.0 \div 1.4$ in winter and their increase up to $1.8 \div 2.4$ in the warm period of year. It is shown also that increase of the Angstrom exponent is caused mainly by the effect of smokes from Siberian forest fires, as well as vegetation fires in spring and autumn seasons. In summer our region is influenced often by the forest fire smokes. The maximum values a observed in May till October correspond to coming of the smoke plumes of the remote Siberian forest fires. The estimates have shown that in April till October in 2010-2017 the average number of days with the effect of forest fire smoke is \sim 43 days, i.e. about 20%. As the aerosol matter in forest fire smoke is characterized by the enhanced values of the organic carbon / elemental carbon ratio OC/EC \sim 2.6÷9, coming of the smoke plumes to our region leads to the increase of the Angstrom exponent values. The increase of a is also observed in the periods of agricultural fires of vegetation in April-May and September. Of course, observed increase of a in warm season up to ~ 2.5 is caused by the growth of absorbing organic components of different chemical composition (Brown Carbon) in aerosol, which are intensively emitted into the atmosphere during the low-temperature smoldering of fuels and biomass (smokes of forest fires, wood heating, etc.) in the form of primary organic aerosol.

The work was supported in part by the Program of the Presidium of the Russian Academy of Sciences No. 51 "Climate change: reasons, risks, subsequences, problems of adaptation and regulation".

P3-19 Sizing of ambient particles from a Single Particle Soot Photometer measurement to retrieve mixing state of Black Carbon at a Regional site of the North China Plain

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The effect of BC-containing particles on atmospheric radiative transfer depends not only on the light absorption of the bare BC skeleton, but also on the enhancement of BC absorption after mixing with other non-BC species through atmospheric aging such as coagulation, condensation and cloud processes. We measured the mixing state of refractory black carbon (rBC) particles using a single particle soot photometer (SP2) on 11-27 July 2013 at a polluted regional site (~60 km to the south of Beijing) of the North China Plain (NCP). To improve retrieval of rBC mixing state, we validate and optimize the optical size $(D_{opt,p})$ of ambient particles derived from SP2 and Mie calculation. The Mie calculation is improved by using the retrieved input parameters (i.e., densities and refractive index (RI) of rBC core and RI of coating materials) rather than prescribed values from literatures. By matching the retrieved $D_{ont n}$ with the measured mobility diameter, we retrieve the densities (~0.3-0.6 g cm⁻³) and refractive indices (from 1.21-0.21i to 1.42-0.42i) of rBC core for thinly coated BC particles at mobility size of 200-350 nm; the refractive index of non-BC (or coating) materials is estimated as 1.42-0i. On the other hand, we validate leading-edge-only (LEO) fit of SP2 calculation not only for the thick-coated BC containing particles, but also for the non-BC (pure scattering) larger particles with saturated scattering signals. It is found that the LEO-fit can be used to retrieve $D_{opt,p}$ at least up to ~600 nm for ambient BC-containing particles, and it can successfully provide $D_{opt,p}$ of ambient non-BC particles only up to ~500 nm. Based on the size information, the average coating thickness (CT) of BC-containing particles (200-350 nm) at the NCP is estimated to be ~41-71 nm, with ~13-16 nm CT for thinly coated (or bare) BC particles and \sim 75-114 nm CT for thickly coated BC particles. During the measurement campaign, the aging rate from thinly coated (or bare) BC to thickly coated BC can reach up to $\sim 21\%$ h⁻¹ around noontime, indicating the fast coating of BC. The mixing state of rBC obtained in this study indicates fast aging process and strong light absorbing capacity of BC particles under the polluted conditions in the NCP.

P3-20 Multi-Wavelength Measurement of Aerosol Optical Properties: Laboratory Intercomparison of In-Situ and Filter-Based Techniques

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Atmospheric aerosol absorption properties play a key role on the Earth radiation balance. Although both in-situ and filter-based instruments have been developed in the last years to measure aerosol optical properties, no reference instrument exists for their determination yet, due to particles complexity and technological issues.

Filter-based methods are the most commonly used, even though multiple scattering and possibly loading effects have to be accounted for. In the Multi-Angle Absorption Photometer (MAAP) and the home-made multi- λ polar photometers PP_UniMI^[1] and MWAA (Multi-Wavelength Absorbance Analyzer^[2]) - this is accomplished by determining the total light transmitted and diffused in forward and back hemispheres and applying radiative transfer models. Opposite, some commercially available instruments as the Aethalometer, the Particle-Soot Absorption Photometer (PSAP), and the Tricolor Absorption Photometer (TAP) are based on light transmission only, and different correction schemes relying on measurements or assumptions on scattering properties and loading effects are needed to obtain absorption properties.

In this work, optical properties of laboratory-generated particles and mixtures were measured at Jülich Forschungszentrum (Germany)^[3]. The main goal was to test the performances of filter-based measurements of aerosol absorption coefficient by the above-mentioned polar photometers. Atomized particles of ammonium sulphate and/or Cabot soot or absorbing aerosol produced via an Inverted Flame Soot Generator were dried and sent in a mixing chamber; both in-situ and filter-based instruments were deployed downstream to retrieve the absorption coefficient of the test samples. Light extinction and scattering coefficients at 450 and 630 nm were obtained by two Cavity Attenuated Phase Shift CAPS PMSSA (Aerodyne Research). An integrating Nephelometer (TSI) measured total and back- scattering coefficients at 450, 550, and 700 nm. A MAAP (Thermo; λ =635 nm) and a TAP (Brechtel; λ : 467, 528, 652 nm) were employed to obtain filter-based aerosol absorption coefficients. At the end of the sampling line, a 47 mm diameter filter holder equipped with a Mass Flow Controller was used to produce aerosol samples to be measured off-line by multi- λ absorption coefficient with PP_UniMi (λ : 405, 532, 635, 780 nm) and MWAA (λ : 375, 407, 532, 635, 850 nm).

In the presentation, a detailed validation of the multi-wavelength MAAP approach against different techniques applied in this study will be reported. Differences in multi-wavelength determination of the absorption coefficient obtained by the multi-wavelength MAAP approach and other methods will be evidenced, considering their role in the assessment of different aerosol components and sources during field campaigns.

[1] Bernardoni . et al. (2017). J. Aerosol Sci. 107, 84–93

[2] Massabò . et al. (2013). J.Aerosol Sci. 60, 34-46

[3] Petzold et al. (2013). Atmos. Meas. Tech. 6, 1141-115

P3-21 A potential reference standard for black carbon absorption measurements: Investigations on the optical properties and morphology of propane-based soot aerosol

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Incomplete combustion leads to the emission of black carbon (BC) aerosol particles, which are considered the second largest climate forcing agent and are associated with health effects. Measuring BC is commonly done by using optical instruments that measure light attenuation through a filter substrate or by opto-thermal methods like photoacoustic spectroscopy. Those methods are used to determine the BC mass concentration by assuming a mass absorption cross-section (MAC). Despite the widespread use of those techniques, there is no preparative BC reference soot standard available to calibrate absorption measurements. Calibration factors for the different absorption techniques need to be linked to a metrological defined reference aerosol and primary BC instrumentation, which is not available. This work is part of an effort to develop a traceable method to determine BC aerosol absorption coefficients.

This work focuses on the optical and morphological characterization of the fresh BC particles. The particles were generated by combustion of propane in a diffusion flame with a mini-CAST 5203C (triple flame, Jing Ltd), using different mixtures of fuel and air; including fuel-lean, stoichiometric, and fuel-rich conditions. The particle number size distributions were measured with a scanning mobility particle sizer (SMPS). A polar nephelometer was used to measure scattering coefficients of the aerosol particles. Absorption was measured by several instruments including multi-angle absorption photometer (MAAP), cavity attenuated phase shift spectrometer (CAPS PMex), photoacoustic extinctiometer (PAX) and aethalometer. This way, optical parameters like single-scattering albedo (SSA) and absorption Ångström exponent (AAE) were retrieved. Morphological properties the particles were investigated by scanning electron microscopy (SEM).

The operating conditions were configured to obtain aerosol particles with geometric mean mobility diameters (GMD) from 25 to 100 nm. The optical measurements showed that the aerosol was rather strongly light absorbing with SSA values spanning from 0.02 to 0.30, at 635 nm wavelength. Fuel-rich mixtures produced the "brightest" aerosol particles, with the highest SSA values (0.20 - 0.30, GMD=100 nm; 0.18 - 0.25, GMD=70 nm). After removing the volatile components from the aerosol using a catalytic stripper at 350 °C, the particles exhibited at least 50% lower SSA values with the maximum value being 0.15 for particles of GMD=100 nm. Stability and reproducibility of the aerosol output by the mini-CAST generator were determined to be in the 6 % over 3 hours range.

In conclusion we could show that the propane combustion soot generator used in this study is a suitable and stable source of fresh BC that can be implemented as a preparative soot aerosol standard for the calibration of soot absorption measurement instruments. Size effects on different filter-based absorption measurement instruments require further investigations.

P3-22 Optical properties of black carbon aggregates with coatings: parallel experimental and numerical computation study

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Light absorbing carbon (LAC), also called black carbon, is pointed out to be the second most contributor to global warming after CO2. Measurement of optical properties of LAC is required to analyze the radiative impacts of this aerosol species. Primary particles of diameters up to 30nm are produced from flames which aggregate to form fractal structures. These aggregates can be purely black carbon in composition depending upon the burning conditions. As the aggregates start to age, their morphology changes. Subsequent nucleation processes can result in the formation of coatings of organic carbon (OC) or sulfate which are additional products of burning. This results in the change of optical properties of the BC aggregates.

Simultaneous numerical and experimental studies are important to improve our understanding of the variation of optical and microphysical properties of coated BC aggregates, which is the key aspect of this study. We have conducted parallel laboratory and numerical studies (based on scattering theory) to calculate and examine the optical properties of both pure and coated BC aggregates

For laboratory measurements, a diffusion flame-based BC generator (mini-CAST 5203C, Jing Ltd, Switzerland) is used at different operating points to generate BC aggregates. Aggregates of mean volume equivalent mobility diameter (DV) between 30nm-160nm are produced by varying the flame equivalence ratio(\emptyset). A Catalytic Stripper is operated at two temperatures to remove the organic coating resulting in pure BC aggregates. The results are divided into cases of 14 operating depending points various upon flame equivalence ratios and mobility diameter1. Polar nephelometer, Multi-Angle Absorption Photometer (MAAP) and Cavity Attenuated Phase Shift extinction (CAPS PMex) are used to measure the scattering, absorption and extinction coefficients, respectively. The experimental SSA varies from 0.02 to 0.3 at different operating points.

For the numerical study of optical properties, a Diffusion Limited Algorithm (DLA) program along with Multi Sphere T Matrix Code (MSTM) is used to design the aggregates and calculate the resulting optical properties. MSTM applies the multiple sphere T matrix method for calculating light scattering properties of a group of spheres. For simulating each laboratory result, we use the experimental value of DV and primary particle size(a). Analyzing the burning conditions for each case, we estimate the suitable fractal dimension (Df) and a constant pre-factor(ka). The simulated aggregates, wavelength, refractive index and range of scattering angles are used as inputs in the Multi Sphere T Matrix Code (MSTM). We found that results from numerical simulations closely matches the experimental results.

1 For more details refer to Saturno et al: A potential reference standard for black carbon absorption measurements: Investigations on the optical properties and morphology of propane-driven soot aerosol. Contribution to ICCPA 2019.

P3-23 Variability in Mass Absorption Cross-section of Black Carbon from Large-Scale Turbulent Diffusion Flames: Sensitivity to Combustion Conditions and Development of a Phenomenological Model

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The mass-normalized absorption cross-section (MAC) of black carbon (BC) is the critical optical property linking radiative forcing by atmospheric BC with its mass loading. For freshly-emitted BC, it is currently thought that MAC likely has a consistent, source-independent value. This notion is discussed in detail in the seminal literature review of Bond & Bergstrom (2006), who reach this conclusion on the justifiable argument that inter-study variability in BC MAC is overshadowed by measurement uncertainties. Bond & Bergstrom (2006) also note however that MAC – specifically the refractive index of BC – is sensitive to the degree of graphitization of BC particles and, hence, the in-flame time-temperature history of BC. The literature data available to Bond & Bergstrom (2006) were generally based on diesel engines (short in-flame residence) and small-scale laboratory flames burning fuels with high sooting propensity. If enhanced graphitization of BC is expected with longer residence times, this suggests that MAC values for larger-scale flames could be greater than the mean value found in Bond & Bergstrom's (2006) review.

This work seeks to address the lack of experimental data for BC MAC from large-scale flames, specifically those representative of gas flaring in the global oil and gas industry. Vertical flames of up to \sim 3 m in length burning a broad range of industry-relevant compositions were created from vertical pipe stacks up to 3" in diameter. Simultaneous measurements of BC absorption and mass were completed with a three-wavelength photoacoustic spectrometer and thermal-optical organic/elemental carbon analyzer. Calibration and measurement uncertainties were rigorously quantified using a Monte Carlo method. Variability in BC MAC, beyond measurement uncertainties, was observed for the studied flames and BC MAC was found to be statistically sensitive to numerous fuel and aerodynamic metrics. These statistically significant parameters were leveraged to develop a phenomenological model that accurately captures the observed variability. The functional form of this model suggests that large-scale flames burning lower molecular weight fuels tend to produce more graphitic and, hence, more strongly-absorbing BC. The derived model reconciles previous field-observations (Weyant et al., 2016) that were thought to be disparate with the MAC value of Bond & Bergstrom (2006) and has important implications for estimates of radiative forcing by BC emitted by gas flaring.

P3-24 Major influence of secondary organic aerosol to lensing effect black carbon absorption enhancement

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Atmospheric black carbon (BC) and light-absorbing organic aerosol (also referred as brown carbon, BrC) have strong effects on the Earth's climate by absorbing direct solar radiation. A better understanding of specific underlying mechanisms is still needed to parametrize the influence of primary emissions and secondary processes on absorption properties. In particular, BC absorption enhancement (E_{abs}) due to internal mixing with other chemical species - so-called lensing effect - is poorly assessed, due to the lack of long-term in situ measurements of both the optical and chemical properties of BC-containing particles. Here, we report results of a three-year continuous field observations conducted from March 2014 to March 2017 at a suburban background station (SIRTA) in the Paris region (France). Submicron nonrefractory aerosol species were measured in near real-time using an aerodyne aerosol chemical speciation monitor (ACSM) and were apportioned using Positive Matrix Factorization (PMF) analysis to identify and quantified major organic aerosol (OA) sources. Light absorption properties of BC and BrC were determined by direct measurements using a 7-wavelength aethalometer equipped with the dual spot technology. Important BrC contribution to the total absorption in the near UV could be attributed to residential wood burning activities in winter and led to significant E_{abs} , independently of internal or external BrC mixing with BC particles. Co-located 24-hy filter-based analyses were also performed by thermo-optical technique to quantify the mass concentration of elemental carbon (EC) in PM25. Absorption enhancement (E_{abs}) of BC-containing particles was obtained using mass absorption coefficient (MAC) ratios calculated between observed (= b_{abs} / [EC]) and expected values for uncoated BC. Results showed that the observed E_{abs} significantly increased with the mass ratio of secondary aerosols to EC, indicating a strong influence of this secondary components on BC absorption enhancement. These findings suggest that SOA could represent one of the most critical chemical species to be considered within climate models.

P3-25 Optical properties of laboratory-generated tar balls

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Tar balls (TBs) are ubiquitous in the troposphere and represent a special particle type emitted from biomass burning. The contribution of tar balls to the mass concentration of atmospheric particles can be significant in the vicinity of biomass burning sources. These particles belong to the family of atmospheric brown carbon (BrC) that can absorb light in the visible range of the solar spectrum. Since the global contribution of BrC to light absorption may be as high as 20 % at 550 nm, and the contribution of BrC absorption in the visible range may be attributed to TBs. On the other hand these particles might also have considerable absorption in the near-infrared spectral region, which is often neglected, since it is usually assumed that in this range the only light-absorbing carbonaceous particles are the black carbon (BC) particles.

In this study tar ball particles were produced in controlled laboratory experiment and their chemical and optical properties were measured. The absorption of these particles in the range between 470 and 950 nm was directly measured with an aethalometer, which is widely used to measure atmospheric aerosol absorption. The scattering coefficient and the number size distribution as well as the elemental composition of the generated particles were also quantified and the optical parameters were calculated from the measured data. We have found that tar balls do absorb red and near-infrared radiation significantly. The absorption coefficient of tar balls at 880 nm is more than 10 % of that at 470 nm. The considerable absorption of red and infrared light by tar balls also follows from their relatively low absorption Ångström coefficient (and significant mass absorption coefficient) in the spectral range between 470 and 950 nm. The estimated contribution of tar balls to the measured absorption at 880 nm was 5–19% at a measurement station in Hungary.

Our results support the previous finding that tar balls may play an important role in radiative transfer processes. Due to the non-negligible absorption of tar balls in the near-infrared region, the absorption measured in the field at near-infrared wavelengths cannot solely be due to soot particles. This also means that the role of BC—a significant fraction of which is derived from fossil fuel combustion (diesel soot)—is likely overestimated in global radiative forcing estimates if the aerosol absorption in the red and near-infrared spectrum is attributed exclusively to BC.

The authors are grateful for the financial support of the GINOP-2.3.2-15-2016-00055 Project through the National Research, Development and Innovation Office, Hungary. This work was supported by the János Bolyai Research Scholarship of the Hungarian Academy of Sciences

P3-26 Dynamic changes of optical and chemical properties of tar ball aerosols by atmospheric photochemical aging

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Following wood pyrolysis, tar ball aerosols were generated from wood tar and separated into polar and nonpolar phases. Chemical information of fresh tar balls was obtained from a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) and single-particle laser desorption/resonance enhanced multiphoton ionization mass spectrometry (SP-LD-REMPI-MS). Their continuous refractive index (RI) between 365 and 425 nm was retrieved using a broadband cavity enhanced spectroscopy (BBCES). Dynamic changes of the optical and chemical properties for the nonpolar tar ball aerosols in NOx-dependent photochemical process were investigated in an oxidation flow reactor (OFR). Distinct differences in the chemical composition of the fresh polar and nonpolar tar aerosols were identified. Nonpolar tar aerosols contain predominantly highmolecular weight unsubstituted and alkyl-substituted polycylic aromatic hydrocarbons (PAHs), while polar tar aerosols consist of a high number of oxidized aromatic substances (e.g., methoxyphenols, benzenediol) with higher O:C ratio and carbon oxidation state. Fresh tar balls have light absorption characteristics similar to atmospheric brown carbon (BrC) aerosol with higher absorption efficiency towards the UV wavelengths. The average retrieved RI is 1.661+0.020i and 1.635+0.003i for the nonpolar and polar tar aerosols, respectively, with absorption Ångström exponent (AAE) between 5.7 and 7.8 in the detected wavelength range. The RI fits a volume mixing rule for internally mixed nonpolar/polar tar balls. The RI of the tar ball aerosols decreased with increasing wavelength under photochemical oxidation. Photolysis by UV light (254 nm), without strong oxidants in the system, slightly decreased the RI and increased the oxidation state of the tar balls. Oxidation under varying OH exposure levels and in the absence of NOx diminished the absorption (bleaching), and increased the O:C ratio of the tar balls. The photobleaching via OH radical initiated oxidation is mainly attributed to decomposition of chromophoric aromatics, nitrogen-containing organics, and high-molecular weight components in the aged particles. Photolysis of nitrous oxide (N2O) was used to simulate NOx-dependent photochemical aging of tar balls in the OFR. Under high NOx condition with similar OH exposure, photochemical aging lead to the formation of organic-nitrates, increased both oxidation degree and light absorption for the aged tar ball aerosols. These observations suggest that secondary organic nitrate formation counteracts the bleaching by OH radical photooxidation to eventually regain some absorption of the aged tar balls aerosols. The atmospheric implication and climate effects from tar balls upon various oxidation processes will be briefly discussed.

P3-27 Infrared-Absorbing Carbonaceous Tar Can Dominate Light Absorption in Heavy-Fuel-Oil PM

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Heavy fuel oil (HFO) is widely used by ships in the open ocean and Arctic, and is known to emit substantial amounts of black carbon and polyaromatic hydrocarbons. However, we show here that those light-absorbing species do not comprise the bulk of the direct climate forcing by HFO emissions. Our characterization of marine-engine emissions shows that a previously unidentified particle type, insoluble and infrared-absorbing tar, dominates total light absorption at low engine loads. Tar particles have a higher fraction of sp³-bonded carbon than BC, and consequently a high Angstrom absorption exponent (AAE) of ~2.0 at wavelengths 370–1000nm. As this tar is refractory, thermal–optical analysis cannot be used to distinguish it from BC; its climate effects are most accurately quantified by direct light-absorption measurements taken at specific wavelengths. Field observations suggest that tar already contributes to accelerated Arctic snow melt, an effect which may be magnified as Arctic shipping continues to intensify.

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